

AD-A086 662

BATTELLE COLUMBUS LABS OH
QUANTUM MECHANICAL STUDIES OF MOLECULAR HYPERPOLARIZARILITIES. (III)

APR 80

F/6 20/5

F49620-78-C-0046

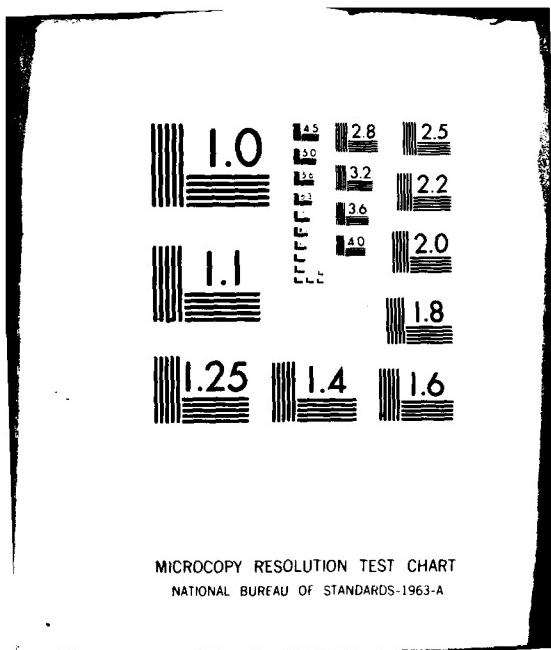
UNCLASSIFIED

AFOSR-TR-80-0466

NL

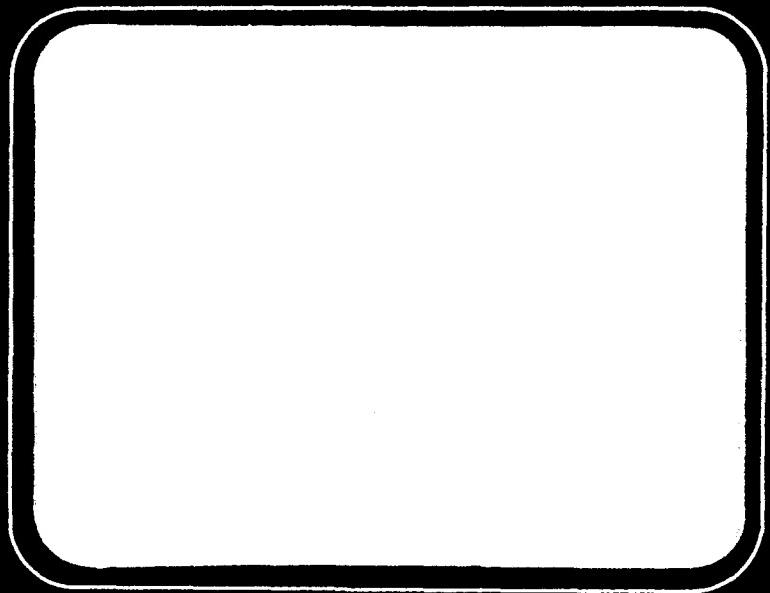
100-412-12

END
DATE
FILED
8-80
DTIC



AFOSR-TR- 80-0466

ADA 086662



(11) AFOSR

(12)

(13) TR-18-0466

FINAL TECHNICAL REPORT

on

(14) 30 APR 1980

QUANTUM MECHANICAL STUDIES OF
MOLECULAR HYPERPOLARIZABILITIES

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

(9) Final Technical
Rept.

April 1980

DTIC
ELECTED
JUL 7 1980
S D
C

(15) F49620-78-C-0046

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMISSION TO DDC
This technical report has been reviewed and is
approved for public release under the EIAW AR 190-12 (7b).
Distribution is unlimited.

A. D. BLOSE
Technical Information Officer

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

407080 set

TABLE OF CONTENTS

	<u>Page</u>
I. DESCRIPTION OF PROBLEM AND RESEARCH OBJECTIVES	1
II. HYPERPOLARIZABILITIES AND NONLINEAR OPTICS	4
III. QUANTUM MECHANICAL PREDICTIONS OF HYPERPOLARIZABILITIES	11
A. Computational Approach.	11
B. Applications.	17
IV. PRESENTATIONS AND PUBLICATIONS	25
V. REVIEW OF RESEARCH ACCOMPLISHMENTS	27
REFERENCES	30

APPENDIX A

MOLECULAR HYPERPOLARIZABILITIES.

I. THEORETICAL CALCULATIONS INCLUDING CORRELATION

APPENDIX B

MOLECULAR HYPERPOLARIZABILITIES

II. A CORRELATED STUDY H₂O

Accession For	
NTIS GRAAI	<input checked="" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	<input type="checkbox"/>
By _____	
Distribution/	
Availability/	
Dist	Available or special

A

FINAL TECHNICAL REPORT

on

Contract F49620-78-C-0046 *ver*

QUANTUM MECHANICAL STUDIES OF
MOLECULAR HYPERPOLARIZABILITIES

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

April 30, 1980

I. DESCRIPTION OF PROBLEM AND RESEARCH OBJECTIVES

The ability of atomic gases, or polar molecular gases oriented by electric fields, to double and triple the frequency of laser radiation is determined by the hyperpolarizability tensors β and γ of the gaseous molecules.⁽¹⁾ Thus, these tensors are becoming increasingly important in a wide variety of real and potential laser applications.⁽²⁻⁴⁾ Such applications include the possibility of producing high frequency, high power laser radiation, utilizing various up-conversion techniques.⁽²⁻⁵⁾

For example, it has been proposed to use selenium vapor to frequency triple CO₂ laser radiation to enable atmospheric transmission⁽⁴⁾, and it has been shown that up-conversion of infra-red laser radiation utilizing two-photon pumped alkali-metal vapor is possible.⁽²⁾ Since the crucial piece of information in each case is the hyperpolarizability of the vapor, the practical development of such techniques is jeopardized by a lack of knowledge of the hyperpolarizabilities of atoms and molecules. Experimental determination of these quantities are difficult, and the few theoretical calculations which

had been made prior to the current project, were not able to even provide order of magnitude estimates of these properties.

Hyperpolarizabilities may be deduced experimentally by direct observation of harmonic generation in gases^(1,6,7) and from measurements of the Kerr effect.^(8,9) The experiments are complicated and the range of uncertainty is sometimes large. Since hyperpolarizability is an atomic or molecular property, it may also be predicted from quantum mechanical considerations. Thus, it is quite important to have reliable theoretical predictions of hyperpolarizabilities to complement the experimental effort, and to provide results, particularly for hyperpolarizability as a function of frequency, for experimentally inaccessible problems.

The objectives of this effort ~~for AFOSR~~ are threefold:

- I) Develop state-of-the-art quantum mechanical methods to predict, from first principles, hyperpolarizabilities of atoms and molecules;
- II) Determine why previous theoretical calculations have not been able to even provide order of magnitude estimates of experimental hyperpolarizabilities; and
- III) Apply the quantum mechanical techniques developed in this work to predict hyperpolarizabilities and non-linear susceptibilities for a number of atoms and molecules of interest.

This effort will provide complementary information to on-going experimental efforts directed toward obtaining hyperpolarizabilities.

To improve the theoretical predictions, four predominant areas have been identified. These are: (1) the basis set problem; (2) the effect of correlation; (3) the sensitivity of the hyperpolarizabilities to geometric

changes due to vibration; and (4) the frequency dependence. In this study we have mostly concentrated on investigating (1), (2), and (3) with the question of frequency dependence to follow once the initial three questions have been resolved. Once an understanding of the elements needed to make accurate calculations is achieved, then a series of large-scale computational studies of several atoms and molecules of special interest could be undertaken.

In our initial study, we have developed computer programs needed to obtain correlated hyperpolarizabilities.^(10,11) We have used these programs to provide the first correlated calculations of hyperpolarizabilities for molecules,⁽¹⁰⁻¹³⁾ we have made the first study of the dependence of the hyperpolarizability on molecular geometry,⁽¹²⁾ and we have determined the type of basis sets that are needed to provide reliable results.^(10,11)

Armed with these components, our initial calculations for the β , χ hyperpolarizabilities for molecules⁽¹⁰⁻¹³⁾ provide significantly better agreement with the observed experimental values⁽¹⁴⁾ than any other theoretical work has been able to achieve. It has been clearly demonstrated that correlation effects are of enormous importance in ab initio theoretical predictions of hyperpolarizabilities. For example, even in the comparatively simple case of NH₃ correlation changes β_{zzz} by a factor of four, and doubles the sum $\beta = (\beta_{zzz} + \beta_{xxz} + \beta_{yy})$. In more polar molecules such as BeO, the correlation effect can be even more dramatic. Equally large effects are found in χ . Also, the extreme geometry dependence of β and χ has been elucidated for the first time. These results, plus a number of additional accomplishments in the program, have set the stage for a rigorous, predictive theoretical approach for hyperpolarizabilities, that should serve to assist in the understanding, and in the experimental interpretations of nonlinear optical processes in gases.

II. HYPERPOLARIZABILITIES AND NONLINEAR OPTICS

The treatment of optical effects in a molecule is based upon the dipole moment induced in the medium when perturbed by monochromatic radiation.⁽¹⁵⁾ The appropriate harmonic perturbation operator is

$$H^{(1)}(\underline{r},t) = -e \sum_{i=1}^N \underline{r}_i \cdot \underline{E}^{(\omega)} \cos \omega t , \quad (1)$$

$$= \lambda h^{(1)}(\underline{r})(e^{i\omega t} + e^{-i\omega t}) , \quad (2)$$

subject to the definitions

$$\lambda = |\underline{E}^{(\omega)}|/2 \quad (3)$$

$$h^{(1)}(\underline{r}) = -e \sum_{i=1}^N \underline{r}_i \cdot \underline{a} . \quad (4)$$

In Equations (1) and (4) N is the number of electrons, $\underline{E}^{(\omega)}$ the field strength vector for frequency ω , \underline{r}_i the position vector for each electron i, and, \underline{a} , a unit vector in the polarization direction.

The induced dipole moment is defined as

$$\underline{\mu}(t) = e \langle \psi | \underline{r} | \psi \rangle \quad (5)$$

where $\psi(\underline{r},t)$ are the eigenfunctions of the time-dependent Schrödinger equation. Normal considerations of time-dependent perturbation theory⁽¹⁵⁾ provide the expansion

$$\psi(\underline{r},t) = \psi^{(0)}(\underline{r},t) + \psi^{(1)}(\underline{r},t) + \psi^{(2)}(\underline{r},t) + \dots . \quad (6)$$

By separating the spatial and time dependent parts of the perturbed wavefunctions, we may obtain from Equation (5), (15)

$$\begin{aligned} \langle \psi | \underline{r} | \psi \rangle = & p_0^{(0)} + p_{\omega}^{(1)} E^{(\omega)} \cos \omega t + p_0^{(2)} (E^{(\omega)})^2 + p_{2\omega}^{(2)} (E^{(\omega)})^2 \cos 2 \omega t \\ & + p_{\omega}^{(3)} (E^{(\omega)})^3 \cos \omega t + p_{3\omega}^{(3)} (E^{(\omega)})^3 \cos 3 \omega t . \end{aligned} \quad (7)$$

The coefficients in Eqn. (7) are electric susceptibilities. The terms that are quadratic and higher in the field strength, are responsible for the non-linear optical effects of a medium, as indicated by the frequency doubling and tripling terms, $\cos 2 \omega t$ and $\cos 3 \omega t$. The main objective of the present study is to investigate the capability of first-principle quantum mechanical predictions of these susceptibilities for molecular gases.

The definitions of the susceptibilities, $p_{m\omega}^{(n)}$, in terms of the spatial functions $\{\phi_{+m}^{(n)}\}$ are

$$p_0^{(0)} = \langle \phi_0^{(0)} | \underline{r} | \phi_0^{(0)} \rangle . \quad (8)$$

$$p_{\omega}^{(1)} = \langle \phi_0^{(0)} | \underline{r} | \phi_{+1}^{(1)} \rangle + \langle \phi_{-1}^{(1)} | \underline{r} | \phi_0^{(0)} \rangle . \quad (9)$$

$$\begin{aligned} p_0^{(2)} = & 1/4 [\langle \phi_0^{(0)} | \underline{r} | \phi_0^{(2)} \rangle + \langle \phi_0^{(2)} | \underline{r} | \phi_0^{(0)} \rangle + \langle \phi_{+1}^{(1)} | \underline{r} | \phi_{+1}^{(1)} \rangle \\ & + \langle \phi_{-1}^{(1)} | \underline{r} | \phi_{-1}^{(1)} \rangle - \langle \phi_0^{(0)} | \underline{r} | \phi_0^{(0)} \rangle (\langle \phi_{+1}^{(1)} | \phi_{+1}^{(1)} \rangle + \langle \phi_{-1}^{(1)} | \phi_{-1}^{(1)} \rangle)] . \end{aligned} \quad (10)$$

$$p_{2\omega}^{(2)} = 1/2 [\langle \phi_0^{(0)} | \underline{r} | \phi_{+2}^{(2)} \rangle + \langle \phi_{-2}^{(2)} | \underline{r} | \phi_0^{(0)} \rangle + \langle \phi_{-1}^{(1)} | \underline{r} | \phi_{+1}^{(1)} \rangle] \quad (11)$$

$$-\langle \phi_0^{(0)} | \underline{r} | \phi_0^{(0)} \rangle \langle \phi_{-1}^{(1)} | \phi_{+1}^{(1)} \rangle] .$$

$$\underline{P}_\omega^{(3)} = 1/4 [\langle \phi_0^{(0)} | \underline{r} | \phi_{+1}^{(3)} \rangle + \langle \phi_{-1}^{(3)} | \underline{r} | \phi_0^{(0)} \rangle + \langle \phi_{+1}^{(1)} | \underline{r} | \phi_{+2}^{(2)} \rangle$$
(12)

$$\begin{aligned} & + \langle \phi_{-2}^{(2)} | \underline{r} | \phi_{-1}^{(1)} \rangle + \langle \phi_0^{(2)} | \underline{r} | \phi_{+1}^{(1)} \rangle + \langle \phi_{-1}^{(1)} | \underline{r} | \phi_0^{(2)} \rangle \\ & - \langle \phi_0^{(0)} | \underline{r} | \phi_0^{(0)} \rangle (\langle \phi_{+1}^{(1)} | \phi_{+2}^{(2)} \rangle + \langle \phi_{-2}^{(2)} | \phi_{-1}^{(1)} \rangle + \langle \phi_0^{(2)} | \phi_{+1}^{(1)} \rangle \\ & + \langle \phi_{-1}^{(1)} | \phi_0^{(2)} \rangle) - (\langle \phi_{+1}^{(1)} | \underline{r} | \phi_0^{(0)} \rangle + \langle \phi_0^{(0)} | \underline{r} | \phi_{-1}^{(1)} \rangle) (\langle \phi_{-1}^{(1)} | \phi_{+1}^{(1)} \rangle \\ & + \langle \phi_{+1}^{(1)} | \phi_{+1}^{(1)} \rangle + \langle \phi_{-1}^{(1)} | \phi_{-1}^{(1)} \rangle) . \end{aligned}$$

$$\begin{aligned} \underline{P}_{3\omega}^{(3)} = 1/4 & [\langle \phi_0^{(0)} | \underline{r} | \phi_{+3}^{(3)} \rangle + \langle \phi_{-3}^{(3)} | \underline{r} | \phi_0^{(0)} \rangle + \langle \phi_{-1}^{(1)} | \underline{r} | \phi_{+2}^{(2)} \rangle \\ & + \langle \phi_{-2}^{(2)} | \underline{r} | \phi_{+1}^{(1)} \rangle - \langle \phi_0^{(0)} | \underline{r} | \phi_0^{(0)} \rangle (\langle \phi_{-2}^{(2)} | \phi_{-1}^{(1)} \rangle \\ & + \langle \phi_{-1}^{(1)} | \phi_{+2}^{(2)} \rangle) - \langle \phi_{-1}^{(1)} | \phi_{+1}^{(1)} \rangle (\langle \phi_0^{(0)} | \underline{r} | \phi_{+1}^{(1)} \rangle + \langle \phi_{-1}^{(1)} | \underline{r} | \phi_0^{(0)} \rangle) . \end{aligned}$$
(13)

These terms have convenient physical interpretations.⁽¹⁵⁾ Equation (8) is the static dipole moment while Equation (9) is the frequency dependent dipole polarizability, which, of course, is also related to the index of refraction. The remaining terms are generally referred to as hyperpolarizabilities, or nonlinear susceptibilities. $\underline{P}_0^{(2)}$, the first nonlinear term in the expansion of the induced dipole moment, determines optical rectification. $\underline{P}_{2\omega}^{(2)}$ defined in Equation (11), leads to second-harmonic generation. The two third-order

terms are respectively responsible for the intensity dependent refractive index and third-harmonic generation. By generalizing the perturbation to include a combination of ac and dc electric fields, additional phenomena like the linear electro-optical effect, dc-induced second-harmonic generation, and the Kerr effect may also be described.

Equations (8-13) are the most appropriate expressions to employ in actual calculations of the coefficients in Equation (7), since the wavefunctions $\phi_{\pm m}^{(n)}$ are defined by variational equations obtained from time-dependent perturbation theory. However, for additional insight, particularly with regard to static ($\omega=0$) hyperpolarizabilities, it is often easier to think in terms of sum over states perturbation formulae^(15,16). With the definition of $h^{(1)}(\underline{r})=h(\underline{r})$ in Equation (4), and ω_{k0} being the excitation energy to state k, Equations (9-11) become,

$$\underline{p}_{\omega}^{(1)} = - \sum_{k \neq 0}^{\infty} \underline{r}_{ok} h_{ko} / [(\omega_{ko} + \omega) + (\omega_{ko} - \omega)] . \quad (14)$$

$$\underline{p}_0^{(2)} = -1/4 \sum_{k \neq 0}^{\infty} \{ 2\underline{r}_{ok} h_{ko} h_{oo} / \omega_{ko} [(\omega_{ko} + \omega) + (\omega_{ko} - \omega)] + \underline{r}_{oo} h_{ok} h_{ko} / [(\omega_{ko} + \omega)^2 + (\omega_{ko} - \omega)^2] \}$$

$$+ 1/4 \sum_{k, \ell \neq 0}^{\infty} \{ 2\underline{r}_{ok} h_{k\ell} h_{\ell o} / \omega_{ko} [(\omega_{\ell o} + \omega) + (\omega_{\ell o} - \omega)] \} \quad (15)$$

$$+ h_{ok} r_{k\ell} h_{\ell o} / [(\omega_{ko} + \omega)(\omega_{\ell o} + \omega) + (\omega_{ko} - \omega)(\omega_{\ell o} - \omega)] \} .$$

$$\underline{p}_{2\omega}^{(2)} = -1/2 \sum_{k \neq 0}^{\infty} \{ \underline{r}_{ok} h_{ko} h_{oo} / [(\omega_{ko} + 2\omega)(\omega_{ko} + \omega) + (\omega_{ko} - 2\omega)(\omega_{ko} - \omega)] \\ + \underline{r}_{oo} h_{ok} h_{ko} / [(\omega_{ko} + \omega)(\omega_{ko} - \omega)] \} \quad (16)$$

$$+ \frac{1}{2} \sum_{k,\ell \neq 0}^{\infty} \left\{ \frac{r_{ok} h_{k\ell} h_{\ell 0}}{[(\omega_{ko} + 2\omega)(\omega_{\ell 0} + \omega) + (\omega_{ko} - 2\omega)(\omega_{\ell 0} - \omega)]} \right. \\ \left. + \frac{h_{ok} r_{k\ell} h_{\ell 0}}{[(\omega_{ko} + \omega)(\omega_{\ell 0} - \omega)]} \right\} .$$

The expressions for the third-order coefficients are very long and will not be reproduced here [see Reference (15) for these].

Another notation is frequently used for the susceptibilities in Eqn. (7), particularly for the static ($\omega=0$) case.⁽¹⁷⁾ The defining expression is a Taylor's series expansion of the energy in the presence of an external field,

$$W(\underline{E}) = W(0) - \mu_i E_i - (2!)^{-1} \alpha_{ij} E_i E_j \\ - (3!)^{-1} \beta_{ijk} E_i E_j E_k \\ - (4!)^{-1} \gamma_{ijkl} E_i E_j E_k E_l \quad (17)$$

The summation over repeated indices is assumed. The quantities μ_i , α_{ij} , β_{ijk} , and γ_{ijkl} are respectively components of the permanent dipole moment, polarizability, and the hyperpolarizabilities. A derivative of Eqn. (17) with respect to a component of \underline{E} defines the expansion of the induced dipole moment which may be compared to Eqn. (7). Some consideration of Eqn. (8) and Eqns. (14-16) shows that in terms of sum-over-state expressions,

$$\underline{\mu} = \lim_{\omega \rightarrow 0} \underline{p}^{(0)} \quad (18)$$

$$\underline{\alpha} = \lim_{\omega \rightarrow 0} \frac{\underline{p}^{(1)}}{\omega} = 2 \sum_{k=0}^{\infty} \frac{r_{ok} h_{ko}}{\omega_{ko}} \quad (19)$$

$$\frac{1}{2} \underline{\mu} = \lim_{\omega \rightarrow 0} \frac{\underline{p}^{(2)}}{\omega} = \lim_{\omega \rightarrow 0} \frac{\underline{p}^{(2)}}{2\omega} = \quad (20)$$

$$\begin{aligned}
 & - 1/2 \sum_{k,l} \{ h_{ok} r_{kl} h_{lo}/(\omega_{ko}-\omega)(\omega_{lo}+\omega) \\
 & + r_{ok} h_{kl} h_{lo}/(\omega_{ko}+2\omega)(\omega_{lo}+\omega) \\
 & + h_{ok} h_{kl} r_{lo}/(\omega_{ko}-\omega)(\omega_{lo}-2\omega) \}
 \end{aligned}$$

Eqn. (20) and similar expressions for $\gamma_{ijk\ell}$ are used to make some comparisons with the frequency dependent results for $\underline{P}_{2\omega}^{(2)}$ and $\underline{P}_{3\omega}^{(3)}$. Since the exciting frequency ω is expected to be comparatively low, often in the infra-red, or visible static predictions for β and γ are not expected to differ substantially from the frequency dependent experimental results. However, by considering an expansion about ω in Eqn. (16) a more formal expression for the frequency dependence can be obtained.

Using the relationship that

$$(a+b)^{-1} = a^{-1} \pm a^{-1}ba^{-1} + a^{-1}ba^{-1}ba^{-1} \pm \dots \quad (21)$$

to terms quadratic in ω/ω_{ko} ,

$$\begin{aligned}
 \underline{P}_{2\omega}^{(2)} &= 1/2\beta + \{ 1/2 \sum_{k,l} h_{ok} r_{kl} h_{lo}/\omega_{ko} \omega_{lo} (\omega/\omega_{ko})(\omega/\omega_{lo}) \\
 &+ 7 \sum_{k,l} r_{ok} h_{kl} h_{lo}/\omega_{ko} \omega_{lo} (\omega/\omega_{ko})(\omega/\omega_{lo}) \}
 \end{aligned} \quad (22)$$

Eqn. (22) demonstrates that all terms linear in (ω/ω_{ko}) vanish. For a frequency ω , chosen in the visible, the ratio of $|\omega/\omega_{ko}|$, when ω_{ko} in an optical transition, is usually small. Hence, the quadratic dependence also attests to the comparatively small difference that would be expected between $\underline{P}_{2\omega}^{(2)}$ and $1/2\beta$.

Defining $\bar{\omega}$ as the lowest optical excitation energy in the molecule, then $|\omega/\bar{\omega}| \geq |\omega/\omega_{k_0}|$ for any k , and $|\omega/\bar{\omega}|^2$ can be factored from Eqn. (22). If the two contributions to $\underline{\beta}$ have the same or different signs, then it also follows that $|7\beta(\omega/\bar{\omega})|^2 \geq$ the second term in Eqn. (22). Hence, some estimate of the frequency dependence in $\underline{\beta}$ can be made using this expression. This gives a percent error in the static $\underline{\beta}$ values to be $\sim 7(\omega/\bar{\omega})^2 \times 100$.

The main thrust of this research program is directed at ab initio quantum mechanical predictions of hyperpolarizabilities. These quantities are difficult to obtain experimentally, and equally difficult to compute from first principle quantum mechanics. The next section discusses the quantum mechanical approach.

III. QUANTUM MECHANICAL PREDICTIONS OF HYPERPOLARIZABILITIES

A. Computational Approach

The quantum mechanical approach to calculating static hyperpolarizabilities is built upon Eq. (17). Either of two routes to the evaluation of the coefficients, μ_i , α_{ij} , β_{ijk} , or $\gamma_{ijk\lambda}$ could be taken. One approach is to evaluate $W(E)$ at a series of small values of the field strength (i.e., the finite-field method), from which a series of finite difference equations can be used to obtain the dipole moment and polarizabilities. The other approach would directly calculate the coefficients by considering expressions obtained from the appropriate order of perturbation theory. Although the second route does not require taking small differences among large numbers, it is more difficult to implement at a high level of sophistication since separate sets of involved computer programs must be developed for each order of perturbation theory. The finite-field method instead supplies all the coefficients from a single computer program by simply evaluating $W(E)$ at enough field strengths. This also offers the bonus that a much higher degree of electron correlation can be incorporated into the computer programs that evaluate $W(E)$ than would be convenient to develop if each quantity, μ , α , β , and γ were to be evaluated separately.

In the finite-field approach, there is also a possibility that a lower order coefficient can be contaminated to some degree by the higher coefficients. To reduce this possibility, one can choose the finite-field strengths symmetrically, such as ± 0.01 so that odd and even combinations of $W(\pm 0.01)$ can be made to eliminate the next term in the expansion from the finite difference equations. This eliminates most of the possible contamination.

The finite-difference equations derived for μ, α, β , and χ are reported in Reference (10), included as Appendix A to this report.

The energies $W(\underline{E})$ can be obtained from the linked diagram theorem of MBPT. (18-22) This is

$$W(\underline{E}) = W_{\text{CHF}}(\underline{E}) + \sum_{k=1}^{\infty} \langle \phi_0(\underline{E}) | V(\underline{E}) [(W_0(\underline{E}) - F(\underline{E}))^{-1} V(\underline{E})]^k | \phi_0(\underline{E}) \rangle \quad (23)$$

when the subscript, L, indicates exclusion to linked-diagrams. The terms in this expression are $W_{\text{CHF}}(\underline{E})$, which is the coupled Hartree-Fock finite-field value, $\phi_0(\underline{E})$, the CHF wavefunction, and $F(\underline{E})$ the sum of one-electron Fock hamiltonians including the external one-electron perturbation of Eq. (1). $W_0(\underline{E})$ is the sum of the field dependent one-electron energies associated with the orbitals composing $\phi_0(\underline{E})$. It is apparent from Eq. (23) that the zeroth-order energy in this expression is the CHF result. In previous work on hyperpolarizabilities of molecules, seldom has even the CHF model been used,^(23,24) instead various uncoupled approaches (UHF) have usually been applied⁽²⁵⁾ due to the computational difficulties encountered. The present predictions start with CHF and include the predominant correlation corrections arising from the linked-diagram expansion in Eq. (23). In this respect, this work is unique in studies of molecular hyperpolarizabilities.

In addition to ignoring electron correlation effects in previous predictions of hyperpolarizabilities, the basis set problem has also received inadequate attention. In a molecular calculation, the basis set is usually chosen to be composed of functions (called Slater orbitals) that are similar

to atomic orbitals of the general form $r^{n-1} e^{-\alpha r} Y_{l,m}(\theta, \phi)$, where r , θ , and ϕ are the usual spherical coordinates, and n , l , and m are the normal quantum numbers. The exponential scale factor, α , referred to as the orbital exponent, reflects the screening of an electron in a given orbital by the interior electrons in the atom or molecule. In practice, when studying polyatomic molecules, an exponential dependence of the form $e^{-\beta r^2}$ is usually preferred because of dramatic simplifications in the computation of molecular integrals. When such functions are used to represent a Slater type function, they are referred to as a contracted Gaussian type orbital (CGTO). In this work, the latter functions are used, with a designation for NH_3 perhaps of $(5s4p3d|4s2p)$ meaning 5s, 4p, and 3d type orbitals are used on the heavy, nitrogen, center, and 4s and 2p functions on each hydrogen atom. All components of a p-function (i.e., p_x, p_y, p_z) or a d-function ($d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{yz}, d_{xz}$) are included when a single p or d is listed in the designation. Hence, $(5s4p3d|4s2p)$ corresponds to 65 CGTO functions for NH_3 .

Basis sets have evolved over the years in molecular quantum mechanics until sets of orbital exponents for the different atoms composing the molecule have become established⁽²⁶⁾ for ordinary energy related properties. That is, the principal term in a field-free hamiltonian is proportional to $1/r$, so these basis sets reflect that dependence. When dipole moments, polarizabilities and hyperpolarizabilities are wanted, the operator dependence is instead r^n , where $n = 1, 2$, or 3 . This places a stringent requirement on the basis sets to be used. Since the molecule itself must be adequately described, a normal $(1/r)$ type energy basis is needed, while, in addition, a description of the long-range dependence of the charge density is crucial to accurately represent an r^n operator.

Since quantum mechanical applications have, until recently, been rather limited in the number of basis functions that could be used (typically ≤ 50 CGTO's at the CHF level, and less if correlation is needed), the size of basis which would have the combination of properties required to adequately describe hyperpolarizabilities has been difficult to achieve.

In order to have reasonable confidence in the capability of a basis set to simultaneously describe the electron density in the energy rich (i.e., $1/r$) region of the molecule, and in the tail (i.e., r^n) region, our initial molecular calculations studied the prediction of hyperpolarizabilities with a series of basis sets for HF by comparing with numerical Hartree-Fock calculations.⁽²⁷⁾ The latter calculations, which are only possible for the α_z , α_{zz} , β_{zzz} , and γ_{zzzz} components, avoids any basis set error since the differential equations of Hartree-Fock theory are solved numerically. Besides being limited to the z-components of the various quantities, this technique is applicable to atoms or diatomic molecules, so its value lies in selected comparisons rather than general use. In this manner, we are able to show that a type of selection scheme for CGTO basis sets^(10,27) appears to be capable of reducing the basis set error for CHF hyperpolarizability predictions to ~ 10 percent. Basis sets so chosen, however, require typically 65-80 functions even for the small molecule isoelectronic sequence HF, H₂O, and NH₃. Such large numbers of basis functions, still sorely test quantum mechanical methods and the efficiency of computer programs, so it is absolutely necessary that the more sophisticated and computer intensive correlated calculations benefit from the most advanced methods possible.

The development of MBPT⁽¹⁸⁻²²⁾ under AFCSR sponsorship,^(10,28-30) has made such correlated calculations possible. (The reader is referred to Appendices A and B, for more detailed information about basis set selection and MBPT methods for evaluating correlation corrections for hyperpolarizabilities.)

Two other theoretical developments in this research should also be mentioned. These developments pertain to infinite-order correlated calculations and the frequency-dependent problem.

Most of our computations in the two years of this program were limited to SDQ-MBPT(4). The acronym means the inclusion of all correlation effects due to single-, double-, and quadruple-excitation diagrams that arise through fourth-order in the linked-diagram expansion. This model is described in detail in Appendix A, and we have established this model to be a highly accurate approach for ab initio correlated calculations.⁽¹³⁾ The sensitivity of hyperpolarizabilities to correlation effects, however, suggested that terms higher than fourth-order might be important for such sensitive properties.

To address this question, a substantial development in the past year has been to generalize the theory and computer programs to carry out CCSD calculations (i.e., coupled-cluster singles and doubles). This model is an infinite order generalization of SDQ-MBPT(4), to which CCSD reduces in fourth-order, permits a consideration of possible contributions of higher order terms. The computer codes are functioning and we have been making applications at this level for the H₂O molecule, but the excessive computer time requirements have prohibited us from obtaining a complete picture at this time. Our current indication is that little change will occur due to these higher-order corrections, but we will reserve judgement until our study is completed.

The other theoretical development we have been pursuing pertains to determining hyperpolarizabilities as a function of frequency. This is being accomplished by employing time-dependent Hartree-Fock theory (also known as the Random Phase Approximation) and calculating the β hyperpolarizabilities at a range of frequencies. This approach has the bonus that a great deal of information about the excited state of atoms and molecules is also obtained from inspecting the resonant frequencies. So far, we have assumed that the correlation corrections to the frequency dependent polarizabilities will be essentially the same as in the static case. Otherwise, the computations would become intractable. We have made some preliminary applications at this level which so far support the assertion that the frequency dependent hyperpolarizability is not too different from the static value unless one is near a resonance when more accurate computational approaches would be required. Like the infinite-order CCSD approach discussed above, this project has necessarily been aborted by AFOSR's untimely failure to continue this research project.

B. Applications

The molecules studied in the two years of this project include Be, HF, H₂O, NH₃, BeO, LiF, and N₂. In Appendices A and B, HF and H₂O are considered in depth. N₂ and Be are discussed in previous reports, so the present discussion will primarily focus on NH₃ with a few additional comments about comparisons among different molecules.

From the viewpoint of a comparison between experiment and theory, NH₃ is a very interesting system. From dc-induced second-harmonic generation experiments, Miller and Ward find the electric susceptibility $\chi_{11}^{(2)} = 10/3(\beta_{zzz} + \beta_{zyy} + \beta_{zxx})$ to be $-209 \pm 5 \times 10^{-33}$ esu/molecule.⁽¹⁴⁾ The previous theoretical calculations at the CHF level, predict -44.4,⁽²⁴⁾ -65.1,⁽²⁴⁾ -19.0,⁽²⁴⁾ -15.6,⁽²³⁾ and -40.8,⁽²³⁾ all in very poor agreement with the experimental result. Besides the poor agreement with experiment, as a basis set improved, the theoretical calculations show a tendency to be in progressively worse agreement with experiment. This is indicated by the fact that the CHF calculations of Lazzaretti and Zanasi obtained -65.1 with a simple double-zeta basis of just 16 CGTO's, while getting -19.0 when they include polarization functions on all atoms which provides a 30 CGTO basis set.⁽²⁴⁾ This behavior is a common trait among hyperpolarizability calculations, reflecting the fact that a small basis set has a sufficiently poor description of the electron density, that gross error cancellation can occur, with the errors in CHF theory partially opposing the errors in the basis set. Once the basis set is somewhat improved, so that a better description of the density is possible, the deficiencies in the CHF

model become more apparent, resulting in even poorer agreement with experiment. However, a 30 CGTO basis is still in no sense adequate for the calculations of properties as sensitive as hyperpolarizabilities. In our work, much better basis sets are used while electron correlation is also properly included.

Using the procedure described elsewhere⁽¹⁰⁾ which enabled us to define basis sets that provide good agreement with numerical Hartree-Fock calculations, we have generated a (5s4p1d|4s2p) basis set for NH₃ (basis A; 53 CGTO) and a (6s4p3d|4s3p) basis set 75 CGTO. The results obtained with these basis sets are shown in Table I. A susceptibility $\chi_{11}^{(2)}$ of -209×10^{-33} esu/molecule corresponds to a $\beta = -72$ in atomic units.

It is apparent from Table I and II that the much superior basis sets of the present work are capable of quite accurate predictions of the dipole moment and polarizability. However, even for these properties, which are not as sensitive to correlation as are the hyperpolarizabilities, there is a significant change between the noncorrelated (CHF) results and the correlated SDQ-MBPT(4) predictions. The dipole moment changes about 6 percent, just as in HF and H₂O, while the polarizability changes by ~9 percent. For these two properties, there is far less difference between the two basis sets than there is due to correlation effects. Notice in particular in Table II the dramatic change in the anisotropy, $\alpha_{11}-\alpha_1$, due to correlation.

The most dramatic effect of basis set and correlation is reserved for the more sensitive hyperpolarizabilities. For example, the change to a more complete, diffuse basis set, causes a factor of two reduction in β_{zzz} which is responsible for basis B predicting a $|\beta|$ that is smaller than in the somewhat poorer basis A, but still the agreement between the CHF results and

TABLE I. COMPARISON OF CHF AND SDQ-MBPT(4) DIPOLE MOMENTS
AND POLARIZABILITIES FOR MOLECULES (ATOMIC UNITS)

Molecule		CHF	SDQ-MBPT(4)	Experiment
HF	μ	0.758	0.709	0.707
	α	4.89	5.58	5.52
H_2O	μ	0.784	0.735	0.724
	α	8.53	9.54	9.64
NH_3	μ	0.614	0.578	0.579
	α	1.1	14.2	14.8
LiF	μ	2.56	2.49	2.49
	α	7.48	9.83	...
BeO	μ	2.96	2.52	...
	α	20.9	29.73	...

experiment is poor. In terms of $x_{11}^{(2)}$, our best CHF calculation predicts -70.8, while for basis A, we obtain -85.8. These are improvements over other CHF calculations, but obviously, even with superior basis sets, there are large effects that contribute to the hyperpolarizabilities that are not yet included.

The largest single effect, we believe, is the effect of electron correlation. This is demonstrated in Table II. In our best basis set, B, correlation causes a factor of four increase in β_{zzz} with a more modest increase in β_{zyy} . The increase in basis A is not as great, but still amounts to a factor of more than two in β_{zzz} . It is not entirely clear why such large effects are observed due to correlation, but it apparently pertains to a much more accurate description of the long-range part of the charge density that is being preferentially sampled by properties like hyperpolarizabilities. Also, the lone pair of electrons on the z-axis is expected to be quite sensitive to correlation effects.

In Table III a comparison of NH₃ with HF and H₂O is presented. Correlation changes β by almost 100 percent of the CHF result for NH₃, while being respectively 28 percent and 50 percent for HF and H₂O. This may be due to the single lone pair in NH₃ contributing its entire effect in one direction while the two pairs in H₂O and three in HF have somewhat opposing effects. Whatever the reason, with correlation our prediction for $x_{11}^{(2)}$ for NH₃ is -138.7×10^{-33} esu/molecule in much better agreement with the dc-induces second harmonic prediction of $-209 \pm 5 \times 10^{-33}$ esu/molecule than all previous calculations as shown in Table III. It is apparent that the agreement can still be improved, but it is certainly evident that only a correlated approach has any hope of successfully predicting hyperpolarizabilities.

TABLE II: EFFECT OF CORRELATION AND BASIS SET ON PREDICTED DIPOLE MOMENT, POLARIZABILITIES, AND HYPERPOLARIZABILITIES OF NH₃ ($r_0 = 1.03\text{Å}$, $\theta_0 = 107.2^\circ$; VALUES IN a.u.)

	CHF			SDQ-MBPT(4)		
	<u>A^a</u>		<u>B^b</u>	<u>A^a</u>		<u>B^b</u>
	<u>A^a</u>	<u>B^b</u>		<u>A^a</u>	<u>B^b</u>	Experiment
$w(o)$	-56.2139	-56.2143		-56.4383	-56.4406	-56.503 ^c ; -56.56 ^d
w_{CORR}	• • •	• • •		0.224	0.226	0.277 ^d
μ	0.619	0.614		0.585	0.578	0.579 ^e
$\alpha_{zz} = \alpha_{ }$	12.79	13.43		14.47	15.43	• • •
$\alpha_{yy} = \alpha_{xx} = \alpha_{ }$	12.45	12.91		13.01	13.59	• • •
$\alpha = 1/3(\alpha_{zz} + \alpha_{yy} + \alpha_{xx})$	12.56	13.08		13.50	14.20	14.82 ^f
$\alpha_{ } - \alpha_{ }$	0.34	0.51		1.46	1.84	1.94; 1.62 ^g
$\beta_{zzz} = \beta_{zyy}$	-14.42 (-13.63) ^h	-7.60		-33.8	-27.8	• • •
$\beta_{yyy} = (\beta_{zzz} + \beta_{zxz} + \beta_{zyy})$	-7.67	-8.50		-7.8	-10.2	• • •
γ_{zzzz}	+12.5 (+12.3) ^h	+9.90		+12.2	+9.4	• • •
$\gamma_{yyyy} = \gamma_{xxxx}$	-29.8	-24.6		-49.4	-48.2	-72.1
$\gamma_{zzyy} - \gamma_{yzzz}$	2740 (2680) ^h	4700		4300	8100	• • •
	780 (770) ^h	1200		1000	1500	• • •
	860	1200		1400	2000	• • •

TABLE II.

- ^a Basis A is (5s3p2d&5s2p), 53 CGTO's.
^b Basis B is (6s4p3d|4s3p), 75 CGTO's.
^{c,d} J. A. Popple and J. S. Binkley, Molec. Phys. 29, 599 (1975); First value in RHF limit plus valence correlation. Second value includes correlation due to the $|s^2$ core on N.
^e A. L. McClellan, Tables of Experimental Dipole Moments, Freeman and Co., 1963.
^f H. J. Werner and W. Meyer, Molec. Phys. 31, 855 (1976).
^g N. J. Bridge and A. D. Buckingham, Proc. R. Soc. A, 295, 534 (1966).
^h Values in parenthesis are obtained from field strengths of 0.005 a.u. A comparison between these values with those obtained at 0.01 a.u. provides some indication of errors due to possible contamination of higher order effects.
ⁱ Reference 14.

TABLE III. COMPARISON OF SDQ-MBPT(4) PREDICTIONS OF THE FIRST HYPERPOLARIZABILITIES IN THE ISOELECTRONIC MOLECULES HF, H₂O, AND NH₃

Molecule	β_{zzz} (a.u.)	β_{yyz} (a.u.)	β_{xxz} (a.u.)	β (a.u.)	$x_{11}^{(2)}$ (10 ⁻³³ esu/molecule)	$x_{11}^{(2)}$ (Expt: 10 ⁻³³ esu/molecule)	Other Theoretical Results for $x_{11}^{(2)}$
HF	-9.7	-0.6	-0.6	-10.9	-31.4	...	-26.1 ^b -55.7 ^b -10.8 ^b
H ₂ O	-9.9	-11.0	-3.7	-23.6	-67.9	-94+4	+90.6 ^c -52.5 ^d -79.2 ^d -21.9 ^d -51.6 ^e -48.0 ^e
NH ₃	-27.8	-10.2	-10.2	-48.2	-138.7	-209+5	-44.4 ^d -65.1 ^d -19.0 ^d -15.6 ^e -40.8 ^e

^a Experimental results are those of Miller and Ward, Reference 14.

^b D. P. Sastry, Chem. Phys. Letters 53, 568 (1978), CHF calculations.

^c S. P. Liebman and J. W. Moskowitz, J. Chem. Phys. 54, 3622 (1971), UCHF calculations.

^d Reference , CHF calculations.

^e Reference , CHF calculations.

The components of the χ hyperpolarizability are similarly observed to be greatly affected by basis set and by correlation. The behavior is rather more predictable than in the case of β , however, since improving the basis set increases the size of χ , and correlation further increases it. The correlation effect on γ_{zzzz} is 72 percent of the CHF result, but even the more diffuse basis contributes this large a percentage change. β on the other hand, tends to become smaller with improvements in basis sets, while becoming larger due to correlation effects. Since the correlation effect is usually larger in a better basis, though, the basis set effect is partially offset when fully correlated calculations are made.

The number in parenthesis in Table 1 show the change incurred when a smaller field strength of 0.005 instead of 0.01 is used. This indicates the degree of contamination remaining in the finite field method. Although there is almost a one unit change in β_{zzz} , it is clear that contamination will have little net effect on the observed results.

IV. PRESENTATIONS AND PUBLICATIONS

"Molecular Hyperpolarizabilities. I. Theoretical Calculations Including Correlation", R. J. Bartlett and G. D. Purvis, Phys. Rev. A, 20, 1313 (1979).

"Molecular Hyperpolarizabilities. II. A Correlated Study of H₂O" G. D. Purvis and R. J. Bartlett, Phys. Rev. A, 00, 000 (1980), in press.

"Molecular Hyperpolarizabilities. III. A Correlated Study of NH₃", R. J. Bartlett and G. D. Purvis, to be published.

"Molecular Applications of Coupled Cluster and Many-Body Perturbation Methods", R. J. Bartlett and G. D. Purvis, Proceedings of Nobel Symposium on Many-Body Theory, Physica Scripta 21, 225 (1980).

"Theoretical Predictions of Hyperpolarizabilities for Molecules", R. J. Bartlett, Nobel Symposium on Many-Body Theory, Lerum, Sweden, June 11, 1979.

"Theoretical Predictions of Molecular Hyperpolarizabilities", R. J. Bartlett, International Symposium on the Quantum Theory of Matter, Palm Coast, Florida, March 12, 1980.

"Coupled Cluster and Many-Body Perturbation Methods with Molecular Applications", R. J. Bartlett, presented at the American Conference on Theoretical Chemistry, Boulder, Colorado, June 1978.

"Studies of Molecular Hyperpolarizabilities with Many-Body Perturbation Theory", G. D. Purvis, presented at the International Symposium on the Quantum Theory of Matter, Palm Coast, Florida, March 16, 1979.

"Many-Body Perturbation Theory and Its Applications to Thermochemistry and Molecular Hyperpolarizabilities", R. J. Bartlett, Dept. of Physics, Ohio University, Athens, Ohio, April 6, 1979.

V. REVIEW OF RESEARCH ACCOMPLISHMENTS

Under Air Force Office of Scientific Research sponsorship, a number of accomplishments have been made in this study that we believe make a significant contribution to the problem of atomic and molecular hyperpolarizabilities, and the related nonlinear optical effects of gases.

- A. This project provides the first studies of molecular hyperpolarizabilities ever attempted which include electron correlation. Molecules studied include, N₂, HF, H₂O, NH₃, BeO, and LiF.
- B. This work has demonstrated that correlation effects are tremendously important in a predictive theory of hyperpolarizabilities. In the case of NH₃, BeO, and LiF, correlation can change the hyperpolarizability by more than a factor of two.
- C. To make state-of-the-art quantum mechanical calculations of hyperpolarizabilities, the theory of many-body perturbation theory (MBPT) has been extended to permit the inclusion of all important correlation effects in hyperpolarizability calculations.
- D. A group of highly efficient ab initio computer programs based upon MBPT, and that can use quite large basis sets, have been developed to make possible reliable calculations of hyperpolarizabilities.

- E. We have also generalized the calculation to include frequency-dependence and to treat the important correlation effects in an infinite-order correlated treatment based upon the coupled-cluster formulation.
- F. For the first time, reasonable agreement between theoretical calculations and second-harmonic generation experiments for $\beta = (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})$ has been achieved. For H₂O, Ward and Miller report $\chi^{(2)}$ to be $-94+4 \times 10^{-33}$ esu/molecule,¹¹ while our predictions give -72 and -80×10^{-33} esu/molecule for the static hyperpolarizability. For NH₃ experiment reports -209×10^{-33} esu/molecule while, our calculations give at $\omega=0$, 138.7×10^{-33} esu/molecule. All previous studies of NH₃ were in much poorer agreement with experiment, often even getting an incorrect sign.
- G. In another investigation, which is also the first of its kind, we have studied the β hyperpolarizability tensor as a function of geometry for H₂O. It is found that β is extremely sensitive to molecular vibrations, with its value changing by nearly 50 percent just from equilibrium to the maximum extent of the zero point vibration, for the symmetric stretch mode (See Appendix B).
- H. From (G), it is apparent that proper account of the sensitivity of hyperpolarizabilities with vibration is important if theoretical and experimental numbers are to coincide.

I. Additional studies have been made to determine the types of basis sets required to obtain reliable higher polarizabilities. This is extremely critical to the theoretical predictions. A comparison with completely numerical coupled Hartree-Fock studies of the HF molecule were undertaken, since these results should entail essentially no basis set error. The types of basis sets used are found to agree with the fully numerical CHF calculations to within ~10 percent (See Appendix A).

REFERENCES

1. P. A. Franken and J. F. Ward, Rev. Mod. Phys. 35, 23 (1963).
2. S. E. Harris and D. M. Bloom, Appl. Phys. Letters 24, 229 (1974).
3. E. A. Stappaerts, S. E. Harris, and J. F. Young, Appl. Phys. Letters 29, 669 (1976); K. S. Krishnan, J. S. Ostrem, and E. A. Stappaerts, Optical Eng. 17, 108 (1978).
4. Report of AVCO Everett Research Laboratory, on frequency tripling CO₂ (10.6 μ) radiation; E. T. Gerry, Final Report, Battelle-Columbus Laboratoties, Durham Operations (1977).
5. I. L. Fabelinskii, Molecular Scattering of Light, translated from Russian By R. T. Beyer, Plenum Press, New York (1968).
6. R. S. Finn and J. F. Ward, Phys. Rev. Letters 26, 285 (1971); J. Chem. Phys. 60, 454 (1974).
7. J. F. Ward and I. J. Bigio, Phys. Rev. A11, 60 (1975).
8. A. D. Buckingham and B. J. Orr, Trans. Faraday Soc. 65, 673 (1969).
9. J. M. Brown, A. D. Buckingham, and D. A. Ramsey, Can. J. Phys. 49, 914 (1971).
10. R. J. Bartlett and G. D. Purvis, Phys. Rev. A20, 1313 (1979); included as Appendix A to this report.
11. G. D. Purvis and R. J. Bartlett, Phys. Rev., submitted; included as Appendix B to this report.
12. R. J. Bartlett and G. D. Purvis, "Molecular Hyperpolarizabilities III. A Study of the NH₃ Molecule", to be published, Phys. Rev.
13. R. J. Bartlett and G. D. Purvis, Proceedings of Nobel Symposium on Many-Body Theory, Physica Scripta 21, 255 (1980).
14. J. F. Ward and C. K. Miller, Phys. Rev. 19, 826 (1979).
15. P. W. Langhoff, S. T. Epstein, and M. Karpus, Rev. Mod. Phys. 44, 602 (1972).
16. J. F. Ward, Rev. Mod. Phys. 37, 1 (1965).
17. A. D. Buckingham and B. J. Orr, Quarterly Reviews 21, 195 (1967).
18. K. Brueckner, Phys. Rev. 97, 1353; 100, 36 (1955); J. Goldstone, Proc. R. Soc. A239, 267 (1957).

19. H. P. Kelly, Adv. Chem. phys. 14, 129 (1969).
20. R. J. Bartlett and D. M. Silver, Int. J. Quantum Chem. Symp. 9, 183 (1975); Phys. Rev. A 10, 1927 (1974).
21. R. J. Bartlett and I. Shavitt, Chem. Phys. Letters 50, 190 (1977); 57, 157 (1978).
22. R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. 14, 561 (1978).
23. G. P. Arrighini, M. Maestro, and R. Moccia, Symp. Faraday Soc. 2, 1293 (1968).
24. P. Lazzeretti and R. Zanasi, Chem. Phys. Letters 39, 323 (1976).
25. J. M. O'Hare and R. P. Hurst, J. Chem. Phys. 46, 2356 (1967); S. P. Lickmann and J. W. Moskowitz, J. Chem. Phys. 54, 3622 (1971).
26. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970); J. Chem. Phys. 55, 3958 (1971).
27. P. A. Christiansen and E. A. McCullough, Chem. Phys. Letters 63, 570 (1979).
28. R. J. Bartlett, Principal Investigator, AFOSR-78-3661.
29. R. J. Bartlett, I. Shavitt, and G. D. Purvis, J. Chem. Phys. 71, 281 (1979).
30. L. T. Redmon, G. D. Purvis, and R. J. Bartlett, J. Am. Chem. Soc. 101, 2856 (1979).

APPENDIX A

Molecular hyperpolarizabilities. I. Theoretical calculations including correlation

Rodney J. Bartlett and George D. Purvis III
Battelle, Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201

(Received 7 June 1979)

Static polarizabilities and hyperpolarizabilities for molecules are investigated at the correlated level. The finite-field, coupled Hartree-Fock theory is used as a zeroth-order approximation, with correlation included by using the linked-diagram expansion and many-body perturbation theory, that includes single, double, and quadruple excitation diagrams. The theory is illustrated by studying the hydrogen fluoride molecule. It is demonstrated that the correlation effect for the hyperpolarizabilities β and γ can be quite large. The average polarizability and dipole moment of HF are in excellent agreement with experiment. The relative importance of the various types of diagrams contributing to electric field properties are discussed. The dependence of the computed hyperpolarizability on basis sets is also investigated.

I. INTRODUCTION

The nonlinear optical properties of gases have been of experimental interest for several years.¹⁻⁷ Recently, a number of real and potential laser applications utilizing the frequency-tripling properties of metal vapors and other atomic gases have been suggested.⁸⁻¹⁰ Similar devices employing polar molecules oriented in an electric field can be envisioned for frequency-doubling applications. The utility of such novel devices will be ultimately determined by properties of the atomic and molecular higher polarizability tensors, but little information on these quantities currently exists.

Hyperpolarizabilities may be deduced experimentally from direct observations of harmonic generation in gases³⁻⁵ and from measurements of the Kerr effect.^{6,7} However, the experiments are difficult and the range of uncertainty is often large. Since hyperpolarizability is a property of a single atom or molecule, it may also be predicted from quantum-mechanical calculations. Hence it is important to have reliable theoretical predictions for higher polarizabilities to complement the experimental efforts.

While some coupled Hartree-Fock (CHF)¹¹ level calculations of atomic hyperpolarizabilities are available, mostly for inert gases,¹² very few *ab initio* calculations of molecular hyperpolarizabilities have been attempted,¹³⁻¹⁶ and none of these has yet shown any kind of agreement with experiment.⁴ The molecular calculations which have been made frequently employ inadequate basis sets or are carried out at the level of uncoupled Hartree-Fock perturbation theory.^{13,17} Only a few previous studies have even used the full CHF method,¹⁴⁻¹⁶ with no work, at all, on molecular hyperpolarizabilities at the correlated level. Recent papers have addressed the question of picking adequate basis sets for polarizabilities,¹⁸⁻²⁰ but the accurate inclusion of correlation effects is

still expected to be a necessity if a reliable predictive theory of hyperpolarizabilities is to be developed. Some recent communications have demonstrated the importance of correlation for the dipole polarizability,^{18,20-22} and one would anticipate an equally large, or even larger, correlation effect for the hyperpolarizabilities.

Recent developments in many-body perturbation theory (MBPT)²³⁻²⁷ and the coupled-cluster approaches (CCA),^{25,28,29} have made it possible to include correlation in a sufficiently tractable manner to include a very large part of the net correlation effect in molecular calculations^{25,30} even though comparatively large basis sets are required in hyperpolarizability determinations.

In the following, we report a study of the hyperpolarizabilities of the HF molecule, considering correlation effects due to single, double, and quadruple excitations.²⁵ HF provides a convenient example for this initial study since a numerical CHF result has been obtained for the parallel components of the second- and third-order polarizability by Christiansen and McCullough,^{16,19} and this result may be used to eliminate some uncertainty in choosing a reliable basis set.

II. HIGHER DIPOLE POLARIZABILITIES

The energy of a molecule in an external field $\vec{\delta}$ may be written in a power series as

$$\begin{aligned} W(\vec{\delta}) = & W(0) - \mu_i \delta_i - (2!)^{-1} \alpha_{ii} \delta_i^2 \delta_j \\ & - (3!)^{-1} \beta_{iij} \delta_i \delta_j \delta_k - (4!)^{-1} \\ & \times \gamma_{ijkl} \delta_i \delta_j \delta_k \delta_l, \end{aligned} \quad (1)$$

where the summation over repeated indices is assumed. δ_i is a component of the external field, μ_i is a component of the permanent dipole, α_{ii} a polarizability, and β_{iij} and γ_{ijkl} are, respectively, the second and third polarizabilities.¹⁻⁴ A component of the total dipole moment, p_i , is obtained

from the derivative $\partial W/\partial \delta_i$, which is composed of the permanent moment and an induced moment due to the higher-order terms.

$$-\left(\frac{\partial W}{\partial \delta_i}\right) = -p_i = \mu_i + \alpha_{ii}\delta_i + (2!)^{-1}\beta_{ijk}\delta_j\delta_k + (3!)^{-1}\gamma_{ijkl}\delta_j\delta_k\delta_l \dots \quad (2)$$

The production of second and third harmonic generation follows from the fact that the $\vec{\beta}$ and $\vec{\gamma}$ in term in Eq. (2) involve products of electric field components. Hence for $\delta_i = \delta_{0i} \sin \omega t$, we have

$$\delta_i^2 = \delta_{10}^2 \sin^2 \omega t = \frac{1}{2} \delta_{10}^2 (1 - \cos 2\omega t),$$

and the $\cos 2\omega t$ term gives rise to frequency doubling.¹ Similarly, the third power in δ is responsible for frequency tripling.¹

The polarizabilities $\vec{\alpha}$, $\vec{\beta}$, $\vec{\gamma}$ are said to be second-, third-, and fourth-order properties, respectively, based on the order of the external field in the energy expansion of Eq. (1), while the permanent dipole moment is first order. It may be shown that a Hartree-Fock wave function will predict a first-order property, like the permanent dipole moment, to a comparatively good accuracy because the first correlation corrections vanish,^{31,32} but there is no similar reason to expect the CHF theory^{11,33} to be adequate for the higher-order properties.^{16,21,22} Furthermore, for even highly accurate first-order properties and especially higher-order properties, correlation must be considered.

III. MANY-BODY PERTURBATION THEORY

The coefficients in Eq. (1) can be obtained directly from perturbation theory or by using finite-field methods. Choosing the latter, temporarily, we may write the Hamiltonian for the perturbed molecule as

$$\mathcal{K}(\vec{\delta}) = \mathcal{K} + \lambda \Omega(\vec{\delta}) = F_0 + V + \lambda \Omega(\vec{\delta}) \quad (3)$$

and

$$F(\vec{\delta}) = F_0 + \lambda \Omega(\vec{\delta}), \quad (4)$$

$$\lambda \Omega(\vec{\delta}) = \lambda \sum_{i=1}^N \omega(i) = -\sum_{i=1}^N \vec{\delta} \cdot \vec{r}(i), \quad (5)$$

$$V(\vec{\delta}) = \sum_{i < j} r_{ij}^{-1} - \sum_i u(i, \vec{\delta}). \quad (6)$$

F_0 is the usual independent particle self-consistent-field (SCF) effective Hamiltonian; hence

$$F(\vec{\delta}) = \sum_i [h(i) + u(i, \vec{\delta}) - \vec{\delta} \cdot \vec{r}(i)] \quad (7)$$

$$u(1, \vec{\delta}) = \sum_j \int \chi_j^*(\vec{\delta}; 2) r_{1j}^{-1} \chi_j(\vec{\delta}; 2) d\tau_s, \quad (8)$$

and in the general case the molecular orbitals $\{\chi_i\}$ are field dependent.

If we are only interested in the SCF solution in the presence of the field, then V in Eq. (3) may be neglected. This defines the CHF model, with the field-dependent solutions

$$F(\vec{\delta}) C_s(\vec{\delta}) = \Delta C_s(\vec{\delta}) \epsilon_s(\vec{\delta}). \quad (9)$$

The molecular orbitals $\chi_s(\vec{\delta})$ are defined as an expansion in terms of an atomic orbital basis set $\{\xi_i\}$:

$$\chi_s(\vec{\delta}) = |\xi_i\rangle C_s(\vec{\delta}). \quad (10)$$

From Eqs. (6)–(9) it follows that

$$F(\vec{\delta}) \Phi_0(\vec{\delta}) = W_0(\vec{\delta}) \Phi_0(\vec{\delta}), \quad (11)$$

where

$$\Phi_0(\vec{\delta}) = \langle \chi_1(1) \cdots \chi_n(n) \rangle, \quad (12)$$

$$W_{\text{CHF}}(\vec{\delta}) = W_0(\vec{\delta}) + \langle \Phi_0 | V(\vec{\delta}) | \Phi_0 \rangle. \quad (13)$$

In the CHF case, the SCF equations are solved for fixed (finite field) values of the field strength $\vec{\delta}$. From these solutions, the CHF energy may be obtained as a function of $\vec{\delta}$ as

$$W_{\text{CHF}}(\vec{\delta}) = \sum_{i=1}^N \epsilon_i(\vec{\delta}) - \frac{1}{2} \sum_{i,j=1}^N \langle \chi_i(\vec{\delta}) \chi_j(\vec{\delta}) || \chi_i(\vec{\delta}) \chi_j(\vec{\delta}) \rangle. \quad (14)$$

The double-bar notation designates the two-electron integral,

$$\langle \chi_p \chi_q || \chi_r \chi_s \rangle$$

$$= \int d\tau_1 \int d\tau_2 \chi_p^*(1) \chi_q^*(2) r_{12}^{-1} (1 - P_{12}) \times \chi_r(1) \chi_s(2). \quad (15)$$

The CHF polarizabilities and hyperpolarizabilities may be derived from second and higher derivatives of $W_{\text{CHF}}(\vec{\delta})$ with respect to the field strength. Alternatively, the induced dipole moment can be calculated from the wave function, Eq. (12), with the polarizability and hyperpolarizabilities obtained as first, second, and higher derivatives of the induced dipole moment. The rigorous equivalence between the dipole procedure and the energy-based procedure depends upon the satisfaction of the Hellman-Feynman theorem for the approximate wave functions.²²

As an alternative to the CHF model, a perturbation expansion of $F(\vec{\delta})$ and $u(\vec{\delta})$ in powers of $\vec{\delta}$ may be made. This procedure, subject to orthonormality of the molecular orbitals, leads to the coupled perturbed Hartree-Fock (CPHF) method.³⁴⁻³⁶ The results of CPHF and CHF are formally the same.¹¹

In order to go beyond the CHF level and include

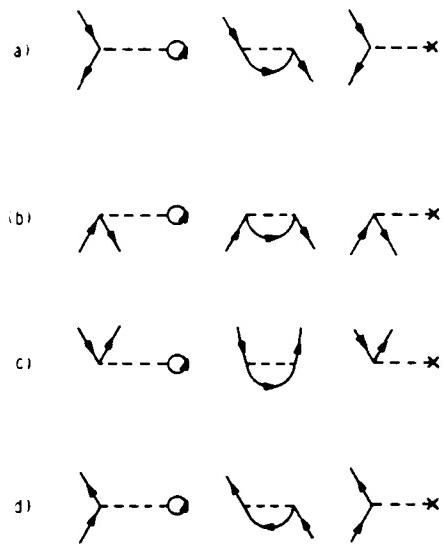


FIG. 1. Single-particle corrections to the energy diagrams. (---x) is the negative of the Fock potential. If occupied and excited one-particle orbitals are determined as SCF solutions at any field strength, then these diagrams component mutually cancel.

effects of correlation, the perturbation $V(\vec{\delta})$ of Eq. (6) needs to be considered in more detail. Including this perturbation, the energy for the perturbed molecule can be obtained from the linked-diagram expansion²⁴ as

$$\begin{aligned} W(\vec{\delta}) = & W_{\text{CHF}}(\vec{\delta}) \\ & + \sum_{k=1}^{\infty} \langle \Phi_0 | V(\vec{\delta}) [W_0(\vec{\delta}) - F(\vec{\delta})]^{-1} V(\vec{\delta})]^k | \Phi_0 \rangle_L. \end{aligned} \quad (16)$$

The terms defined by the summation in Eq. (16) are said to be the correlation corrections to the energy for a given field strength. Just as in the zero-field case, by solving the SCF equations in the presence of the field as in Eqs. (8)–(10), the SCF cancellations shown in Goldstone-diagram form in Fig. 1 (---x is the negative of the Fock

$$\begin{aligned} W_{2,0}(E_x) = & \frac{1}{2}\alpha_{xx} = \langle \Phi_0 | x R_0 x | \Phi_0 \rangle + \langle \Phi_0 | x R_0 (x - W_{1,0}) R_0 V | \Phi_0 \rangle + \langle \Phi_0 | V R_0 (x - W_{1,0}) R_0 x | \Phi_0 \rangle \\ & + \langle \Phi_0 | x R_0 (V - W_{0,1}) R_0 x | \Phi_0 \rangle + \dots \end{aligned} \quad (21)$$

The first term on right in Eq. (21), $W_{2,0}$, is given by the uncoupled Hartree-Fock (UCHF)¹⁷ approximation [Fig. 2(A)], which is

$$W_{2,0} = \sum_{i(\text{occ})} \sum_{e(\text{unocc})} \frac{\langle x_i^0 | x | x_e^0 \rangle}{\epsilon_i^0 - \epsilon_e^0}, \quad (22)$$

while the higher terms involve the field-independent perturbation $V(0)$. The Goldstone diagrams

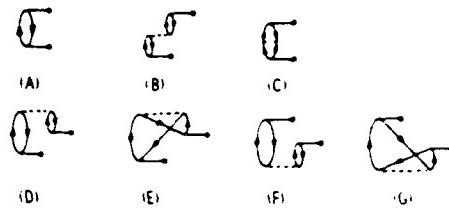


FIG. 2. Zeroth- and first-order relaxation diagrams for a second-order property. These terms are all included in a CHF calculation for a second-order property.

potential) are still maintained, so that no diagrams containing these parts are required.

The coefficients in Eq. (1) are given as derivatives of $W(\vec{\delta})$ with respect to field strength. In the finite-field approach, $W(\vec{\delta})$ must be computed for several field strengths to allow the determination of the polarizabilities, which requires taking small differences between large terms. If the differentiation is made initially, separate linked-diagram expansions for μ , α , β , γ , etc., in terms of the zero-field SCF orbitals [$\chi_p(0) = \chi_p$, $\epsilon_p(0) = \epsilon_p$], can be used to evaluate the small polarizabilities directly.

In the latter case, ordinary double perturbation theory gives

$$W = W_0 + \sum_{n=0}^{\infty} \langle \Phi_0 | (V + \lambda \Omega) \times [(W_0 - F_0)^{-1} P(V + \lambda \Omega - \Delta W)]^n | \Phi_0 \rangle \quad (17)$$

and, for some component S_x ,

$$\begin{aligned} W(S_x) = & W_0 + (W_{1,0} + W_{1,1} + W_{1,2} + \dots) S_x \\ & + (W_{2,0} + W_{2,1} + W_{2,2} + \dots) S_x^2 + \dots. \end{aligned} \quad (18)$$

$$W(S_x) = W_{0,0} + W_{1,0} S_x + W_{2,0} S_x^2 + W_{3,0} S_x^3 + \dots \quad (19)$$

Considering a second-order property for illustration, with the definition

$$R_0 = P(W_0 - F_0)^{-1} P, \quad (20)$$

where P is the projector for the orthogonal complement to Φ_0 ,

for second order in an external field and for zeroth and first order in the two-electron perturbation $V(0)$ are shown in Fig. 2. The symbol (---●) indicates interaction with the external field.

It is important to recognize that even though diagrams (B)–(G) of Fig. 2 involve a two-electron vertex, these diagrams and selection of others in all higher orders in $V(0)$ are included^{27,34} in the

CHF results or in the perturbation-theory-equivalent CPHF.^{15,16} At least in the static case these terms should *not* be considered as correlation corrections. These terms arise, instead, from the effective Fock potential $u(i)$, now written in terms of perturbed orbitals, which reflects the *relaxation* of the orbitals to the external perturbation.¹⁴ Beyond first order in $V(0)$, additional diagrams arise which are *not* included in CPHF,^{14,17} and these terms constitute true correlation corrections. In the finite-field approach, all terms which arise from derivatives of the summation in Eq. (16) are actual correlation corrections, while the initial CHF calculation provides the zeroth- and first-order energy corrections, subject to the field-dependent orbitals. (CPHF is the static equivalent of time-dependent Hartree-Fock theory or the random-phase approximation, which is similarly recognized to sum selections of many-body propagator diagrams to all orders.^{38,39} In the time-dependent context, the terms so summed are frequently referred to as "dynamic" correlation.³⁹)

Even though the direct determination of the polarizabilities is a distinct advantage, it offers the disadvantage that separate sets of programs must be written to evaluate the diagrams for each order in the external perturbation, while the finite-field method allows *all* polarizabilities to be obtained from simply executing "enough" energy calculations at a series of field strengths. This also permits one to exploit the theories and programs that have been developed for the usual correlation problem²⁵ which typically offer a much more sophisticated level of treatment for the correlation than would be convenient to develop for each individual order in an external perturbation. Also, the dichotomy into correlation and

relaxation effects is transparent for the finite-field method.

IV. NUMERICAL RESULTS

In the finite-field methods, it is necessary to obtain the various polarizability components from formulas for the energy or dipole moment. In the present work, either procedure may be used at the CHF level, since $\Phi_i(\delta)$ satisfies the Hellmann-Feynman theorem, but derivatives of $W(\delta)$ will be used for the correlation corrections. By considering Eq. (1), it may be shown that the finite-difference formulas listed in Table I hold for the various polarizabilities. Each of these formulas is obtained by excluding all even or odd terms in Eq. (1) by using positive and negative field strengths of the same magnitude. This ensures that the contamination from the next higher term in the power series is completely removed, leaving only the next higher term of the same type (i.e., even or odd), which is about four orders of magnitude smaller (at the field strengths used here) than any polarizability being determined. Hence, essentially no error is anticipated from higher polarizability contamination. At the same time, however, field strengths of adequate size must be used to ensure that significant energy differences are obtained. In this work field strengths of 0.0, 0.01, and 0.02 a.u. are found to be suitable.

The formulas in Table I are general, but if some symmetry is present, formulas I.3 and I.6 become much simpler. If the molecule has a rotation axis, with i representing the direction of this axis, and j is perpendicular to i , group-theoretical considerations show that the components β_{iijj} , σ_{ii} , γ_{iiji} , and γ_{iiji} are vanishing at zero field strength. This results in particularly simple formulas for

TABLE I. Energy formulas for finite-field calculations of dipole moments, polarizabilities, and hyperpolarizabilities.*

Odd order	
$\mu_i \delta_i = -\frac{1}{2} [W(\delta_i) - W(-\delta_i)] + \frac{1}{12} [W(2\delta_i) - W(-2\delta_i)] + O(\delta)$	(1)
$\beta_{iijj} \delta_i^3 = \frac{1}{2} [W(2\delta_i) - W(-2\delta_i)] + [W(\delta_i) - W(-\delta_i)] + O(\delta)$	(2)
$\beta_{jjj} \delta_i^2 \delta_j - \beta_{iijj} \delta_i \delta_j^2 = -[W(\delta_i - \delta_j) - W(-\delta_i + \delta_j)] + [W(\delta_i) - W(-\delta_i)] - [W(\delta_j) - W(-\delta_j)] + O(\delta)$	(3)
Even order	
$\alpha_{ii} \delta_i^2 = +\frac{1}{2} W(0) - \frac{1}{4} [W(\delta_i) + W(-\delta_i)] + \frac{1}{12} [W(2\delta_i) + W(-2\delta_i)] + O(\epsilon)$	(4)
$\gamma_{iiji} \delta_i^4 = +\frac{1}{4} [W(\delta_i) + W(-\delta_i)] - [W(2\delta_i) + W(-2\delta_i)] - 6W(0) + O(\epsilon)$	(5)
$+\frac{1}{2} \gamma_{iiji} \delta_i^3 \delta_j^2 - 2\alpha_{ii} \delta_i \delta_j^3 - \frac{1}{4} \gamma_{iiji} \delta_i^2 \delta_j^2 + \gamma_{iiji} \delta_i^2 \delta_j^2 = -[W(\delta_i - \delta_j) + W(-\delta_i + \delta_j)] + [W(\delta_i) + W(-\delta_i)] + [W(\delta_j) + W(-\delta_j)] - 2W(0) + O(\epsilon)$	(6)

* For a molecule with a rotation axis in the direction i , α_{ii} , β_{iiji} , γ_{iiji} , and γ_{iiji} will be zero by symmetry.

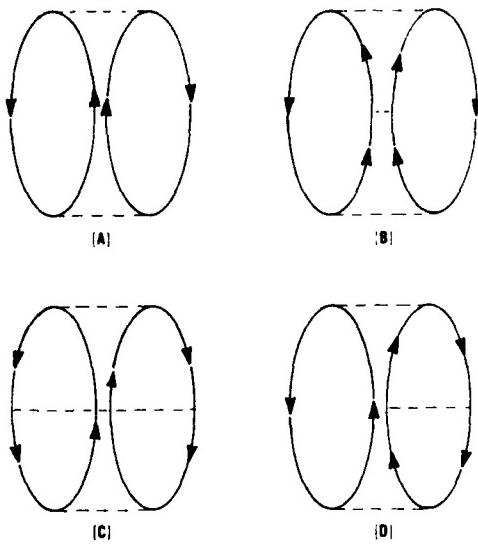


FIG. 3. All second- and third-order correlation diagrams provided that SCF (CHF) orbitals are used for the occupied and excited one-particle states. Antisymmetrized vertices are assumed in these diagrams.

the nonvanishing components.

The finite-field correlation corrections included are shown as antisymmetrized diagrams in Figs. 3-6, where it is understood that the hole and particle lines are field dependent (or "dressed") and that finite differences of these quantities must be taken before the polarizabilities are obtained. (See Refs. 27 and 40 for the rules and algebraic

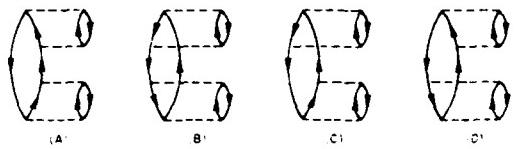


FIG. 4. All single-excitation fourth-order diagrams provided that SCF (CHF) orbitals are used for the occupied and excited one-particle states. Antisymmetrized vertices are assumed.

formulas corresponding to these antisymmetrized diagrams.)

These diagrams consist of all terms that occur through fourth-order in the correlation, subject to field-dependent SCF orbitals that would arise due to configuration-interaction (CI) single, double, and quadruple excitations.²⁵ Triple excitations also contribute in the fourth-order energy, but these are excluded.

It is well known that CI-type single excitations are quite important in determining properties other than the energy, since operators such as $\hat{S} \cdot \vec{r}$, will mix single excitations directly with an SCF unperturbed wave function. In the present work, the predominant effect of single excitations is introduced by means of the initial CHF calculations, which, as described in Sec. III, is responsible for summing a series of diagrams involving such single-excitation vertices as occur in Fig. 2 (i.e., $\hat{\pi}^\alpha$) to all orders. This "dresses" the hole and particle lines involved in Figs. 3-6. The remaining single excitations accounted for by Fig. 4 involve the smaller effect of single excitations of

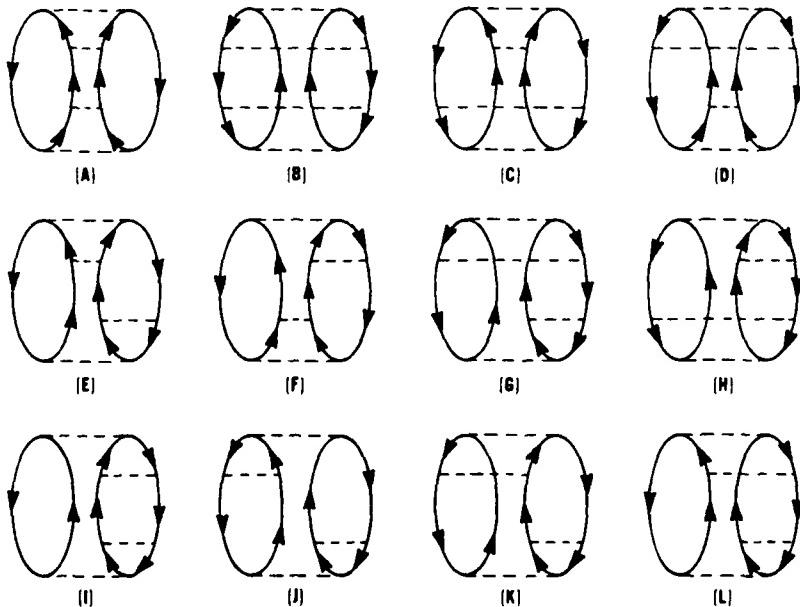


FIG. 5. All double-excitation fourth-order diagrams provided that SCF (CHF) orbitals are used for the occupied and excited one-particle states. Antisymmetrized vertices are assumed.

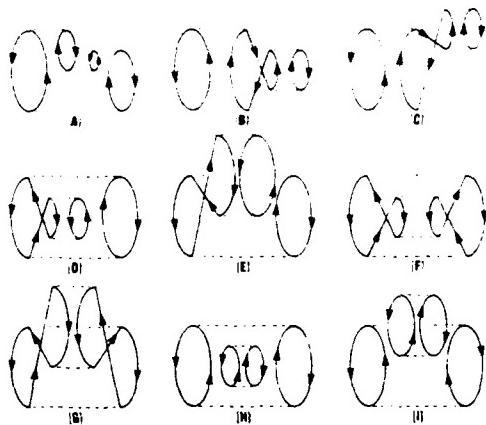


FIG. 6. All quadruple-excitation fourth-order diagrams, provided that SCF (CHF) orbitals are used for occupied and excited one-particle states. Unlinked diagrams (H) and (I) do not contribute to the correlation energy. Antisymmetrized vertices are assumed.

dressed lines that enter into the fourth-order energy only by interacting through dressed double excitations. The very high-order coupling of the first category of single-excitation effects with correlation due to double and quadruple diagrams by using "dressed" hole and particle lines is one of the additional advantages of the finite-field-based methods.

The basis set for the present study of HF is chosen essentially following the prescription of Christiansen and McCullough (CM).¹⁹ We start from Dunning's⁴¹ 5s3p contraction of Huzinaga's⁴² 9s5p basis set for fluorine, and Dunning's 3s contraction for hydrogen Slater exponent 1.2. These functions are augmented by a two-Gaussian fit to a d-STO for F with exponent 3.358, and a two-Gaussian fit to a p-STO, exponent 2.082 for H.⁴³ This results in a 5s3p1d/3s1p initial basis set. This basis is then augmented in a "well-tempered"

fashion. The smallest exponent for each l quantum number per atom is multiplied by 0.4 to obtain a new, diffuse function to assist in describing the polarizability. The resulting basis 6s4p2d 4s2p is expected to be adequate to describe the dipole polarizability. To also attempt to account for the higher polarizabilities, the new exponent is again multiplied by 0.4 to add another p and d function on F, and an s and p function on H. Finally, the most diffuse d exponent on F was again multiplied by 0.4 and this function added to the basis set. We also consider the addition of an extra diffuse s function on F and the exclusion of the most diffuse s and p on H and the d function on fluorine. This provides four different basis sets.

A GTO basis set similar to these has been shown to account for the numerical CHF results for μ_{ee} , α_{ee} , β_{eee} , and γ_{eeee} to within a few percent.¹⁹ However, those authors were unable to reduce the error in the CGTO value for β_{eee} below 7%. When we attempted to use their basis set, with all six possible Cartesian components of the d functions, xx , yy , zz , xz , yz , xy (CM use only the five normal d -function components), we found an approximate linear dependency which made our correlated calculations unstable. We were able to resolve this problem and also substantially reduce the error in the SCF β_{eee} component by choosing a tighter d -polarization function on F (STO $\xi = 3.358$ compared to $\xi = 2.25$ for CM) and then adding an additional diffuse d function to the F atom. Both the tight and diffuse d functions seem to be important as illustrated in Table II. Using a tight d function while excluding the most diffuse d -function (bases A and B) results in a β_{eee} that differs from the numerical result by 11%. In the CM basis, which has a very diffuse d function but excludes a tight polarization d function, a similar error in β_{eee} occurs. By combining both, as in bases C and D, this error is greatly reduced.

The difference between bases C and D is the

TABLE II. Comparison of CHF results for HF in various basis sets with numerical CHF. ($R = 1.7328$ bohrs; values in a.u.)

Basis set (GTO)	$W(0)$	μ^*	α_{ee}	β_{eee}	γ_{eeee}
CM (6s5p3d/4s3p) ^b	-100.0535	0.759	5.80	-9.0	310
A (6s5p3d/5s3p) ^c	-100.0563	0.757	5.72	-9.3	250
B (7s5p3d/5s3p) ^c	-100.0563	0.757	5.72	-9.2	260
C (6s5p4d/4s2p) ^c	-100.0563	0.759	5.73	-8.4	250
D (6s5p4d/5s3p) ^c	-100.0565	0.758	5.76	-8.5	290
Numerical CHF ^b	-100.0706	0.756	5.76	-8.3	320

^a Coordinate system is chosen such that dipole moment (F^+H^-) is positive.

^b Results of Ref. 16.

^c Basis sets A, B, C, and D use all six Cartesian Gaussian d -orbital functions xx , yy , zz , xy , yz , and xz .

TABLE III. Effect of correlation and basis set on predicted dipole moment, polarizability, and hyperpolarizabilities of HF. ($R = 1.7328$ bohrs; values in atomic units.)

	CM ^a	A^b	B^c	CHF	D^d	A^b	B^e	SDQ-MBPT(4)	C^d	D^e	Expt.
$W(0)$	-100.0535	-100.0563	-100.0563	-100.0563	-100.0565	-100.0530	(-100.3287) ^f	-100.3061	-100.3035	(-100.386) ^g	(-100.448) ^{h,i}
W_{corr}	-0.247	(-0.272) ^f	-0.250	-0.247	(-0.315) ^j
μ	0.759	0.7568	0.7569	0.7585	0.7580	0.7076	0.7082	0.7097	0.7089	0.7071	(-0.377) ^k
$\alpha_{xx} = \alpha_{yy}$	5.80	5.72	5.73	5.76	5.76	6.36	6.31	6.32	6.39	6.39	...
$\alpha_{yy} = \alpha_{xx} = \alpha_1$...	4.45	4.45	4.51	4.48	5.13	5.11	5.22	5.18	5.18	...
$\alpha = \frac{1}{2}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$...	4.87	4.87	4.92	4.89	5.54	5.51	5.59	5.58	5.58	(5.52) ^l
$(\alpha_{ii} - \alpha_1)$...	1.27	1.27	1.22	1.28	1.22	1.20	1.10	1.21	1.21	(1.32) ^m
β_{xxx}	-9.0	-9.3	-9.2	-8.4	-8.5	-11.0	-10.8	-9.2	-9.7	-9.7	...
$\beta_{xxx} = \beta_{yyy}$...	-0.4	...	0.0	0.0	-1.2	...	-0.6	-0.6	-0.6	...
$\beta = (\beta_{xxx} + \beta_{yyy} + \beta_{zzz})$	-10.1	...	-8.4	-8.5	-8.5	-13.3	...	-10.4	-10.9	-10.9	...
γ_{zzzz}	γ_{zzz}	230	260	250	280	350	350	340	390	390	...
γ_{yyzz}	...	70	...	80	80	130	130	130	140	140	...

^a(6s5p3d/4s3p). Basis of Ref. 16.

^b(6s5p3d/5s3p). Most diffuse s and d on F is excluded. Correlation calculations freeze $F(1s^2)$ electrons and drop the five highest-lying excited orbitals.

^c(7s5p3d/5s3p). Most diffuse d on F excluded. All electrons are correlated and no excited orbitals are dropped.

^d(6s5p4d/4s2p). Most diffuse s on F and diffuse s, p on H excluded. $F(1s^2)$ frozen and highest virtual orbitals dropped in correlated calculations.

^e(6s5p4d/5s3p). Diffuse s on F excluded. $F(1s^2)$ frozen and highest virtual orbitals dropped in correlated calculations.

^fAll electrons are correlated.

^gP. E. Cade and W. M. Itlo, J. Chem. Phys. 47, 614 (1965), corrected for an estimated -0.082 relativistic energy and modified to exclude correlation involving the $F(1s^2)$ core electrons.

^hTotal nonrelativistic energy including the $F(1s^2)$ contribution.

ⁱValence correlation energy. SCF limit result is -100.3706 (Ref. 16).

^jTotal correlation energy.

^kJ. S. Mounter and W. Klemperer, J. Chem. Phys. 52, 6033 (1970).

^lReference 18. Corrected for zero-point vibration as in this reference.

^mJ. S. Mounter, J. Chem. Phys. 56, 5409 (1972).

TABLE IV. Contributions of different diagrams to dipole moment, polarizability, and hyperpolarizabilities of HF. (Basis set *D*; $R = 1.7328$ bohrs; values in atomic units.^a)

	CHF	Second order	Third order	Fourth order				SDQ-MBPT(4)	CHF + SDQ-MBPT(4)
				Single	Double	Quad.	Total		
$W(0)$	-100.05647	-0.24480	+0.00156	-0.00241	-0.00347	+0.00205	-0.00383	-0.24706	-100.30353
μ_x	0.7580	-0.0478	+0.0072	-0.0058	-0.0051	+0.0024	-0.0085	-0.0491	0.7089
$\alpha_{xx} = \alpha_u$	5.76	+0.688	-0.230	+0.123	+0.079	-0.026	+0.176	+0.63	6.39
$\alpha_{yy} = \alpha_i$	4.48	+0.826	-0.332	+0.145	+0.080	-0.014	+0.206	+0.70	5.18
β_{xx}	-8.48	-0.72	+0.49	-0.7	-0.4	+0.13	-0.97	-1.2	-9.7
$\beta_{yy} = \beta_{zz}$	-0.03	-0.64	+0.51	-0.3	-0.2	+0.03	-0.47	-0.6	-0.6
$\beta = (\beta_{xx} + \beta_{yy} + \beta_{zz})$	-8.54	-2.0	+1.51	-1.3	-0.8	+0.20	-1.90	-2.4	-10.9
γ_{xax}	280	110	-60	50	20	-10	+60	120	390
γ_{yay}	80	60	-30	20	10	0	30	60	140

^a Correlation involving the core is not included.

exclusion of the most diffuse *s* and *p* functions on H. This is seen to have almost no effect on β while having a somewhat larger effect on γ_{xax} . The observation that the diffuse H *s* and *p* functions have only a small effect is partially due to the fact that the diffuse region of the charge cloud is already accounted for by the other highly diffuse functions on F. However, γ_{xax} is usually larger the more diffuse functions that are included in the basis, as supported by the results of bases sets C and D.

It is clear from Table II that good agreement with the numerical results for μ_x , α_{xx} , β_{xx} , and γ_{xax} can be achieved with the present basis sets. It does not necessarily follow that the other components of $\vec{\alpha}$, $\vec{\beta}$, and $\vec{\gamma}$ are as well described or that this basis is entirely adequate for the correlation corrections to the polarizabilities, but the good agreement with the numerical results for the parallel components at least provides an indication that the final correlation corrections to the different polarizabilities should be indicative of the size of the true correlation corrections, which is the primary objective of this study.

In the present correlated calculations, all the single, double, and quadruple excitation diagrams that arise through fourth order in the $V(\vec{G})$ perturbation are included. This model will be referred to as SDQ-MBPT(4). These diagrams are evaluated at various field strengths, from which the equations of Table I are used to provide the different polarizabilities.

To carry out such finite-field calculations successfully, it is necessary to ensure about eight-decimal-place accuracy in all computations, from the initial molecular integrals to the actual diagram evaluation. The current computations employ the MBPT program system developed at Battelle.⁴⁴ Results for the effect of correlations on various properties are shown in Table III.

The $6s5p4d/5s3p$ basis set is seen to be capable of providing about 78% of the observed field-free valence-shell correlation energy. This is consistent with other calculations, where we have shown that a $5s3p1d/3s1p$ basis typically accounts for three-quarters of the valence-shell correlation energy,^{25,45} since the remaining functions in the current bases are generally too diffuse to contribute much to the field-free correlation effect. On the other hand, correlation involving the normal and diffuse functions is important in the presence of the field, so some balance between a reasonable description of the valence-shell correlation and the long-range tails of orbitals is still expected to be significant in obtaining good correlated results for polarizabilities.

The effects of correlation on the other properties

listed in Table III vary from about 7% for the dipole moment to 12% for the polarizability, and a rather dramatic change of about 22% for the β hyperpolarizability. A similarly large change is observed for the γ_{zzz} component of the hyperpolarizability of 30%. The correlated dipole moment and polarizability are found to be in excellent agreement with experiment, although the anisotropy is somewhat farther away. The hyperpolarizabilities seem to be significantly affected by correlation, and although this is only a single molecule out of many, it suggests that a theoretical approach that attempts to predict and explain the experimental values for hyperpolarizabilities must definitely take into account the effects of correlation.

In Table IV are listed the individual correlation corrections for HF which are of some interest in answering questions about the order of perturbation theory needed to get converged correlated answers as well as the effect of the different types of diagrams. It is apparent that most of the correlation correction is obtained from just the second-order energy diagrams. In fact, a comparison of the second-order results with the SDQ-MBPT(4) values demonstrates that there is not too much change due to the third- and fourth-order diagrams, which are of opposite sign. In general, the fourth-order terms have a somewhat larger magnitude than third order, further augmenting the second-order result. This is particularly true of β_{zzz} . This behavior has also been observed in studies of molecular correlation energies,²⁴ as illustrated currently by $W(0)$ for the HF molecule. At first sight, this may cause some reservations, but comparison²⁵ between the DQ-MBPT(4) model for the correlation energy with the infinite-order sum of double and quadruple excitation diagrams normally known as the coupled-cluster-doubles (CCD)²⁶ model shows agreement to within a millihartree for a large group of atoms and molecules. Hence even though fourth order is larger than

third order for this example, it does not necessarily follow that higher-order terms will be important. However, the very small differences involved in finite-field calculations might be more likely to be affected by higher-order terms; hence this question should be borne in mind. We will resolve this point in future work.

For each property except the energy, the single-excitation diagrams provide a larger fourth-order contribution than the double-excitations, while the quadruple excitations are typically a factor of 2 to 3 smaller than the fourth-order double-excitation contribution. This reflects the residual unimportance of single-excitation terms for properties dependent upon one-electron operators, even though this type of single-excitation contribution only appears (because of Brillouin's theorem) in the fourth-order energy via their coupling through double excitations. The predominant single-excitation effect, as discussed previously, is included at the CHF level. Triple-excitation diagrams also occur in fourth order and are likely to be somewhat more important than the quadruple excitations. These probably provide a correction with the same sign as the fourth-order single- and double-excitation diagrams. The relative unimportance of the quadruple excitations plus the fact that the quadruple and triple excitations should have an opposite effect on a polarizability suggest that a limitation to single- and double-excitation diagrams possibly summed to all orders should provide reliable results for these properties, if a well-chosen, well-balanced basis set is used.

ACKNOWLEDGMENTS

The authors appreciate many helpful comments from I. Shavitt. The authors also appreciate E. McCullough's providing us with details about the GTO basis sets used in Ref. 19. This work is supported by the Air Force Office of Scientific Research under Contract No. F49620-78-C-0046.

- ¹P. A. Franken, and J. F. Ward, *Rev. Mod. Phys.* **35**, 23 (1963).
²I. L. Fabelinskii, *Molecular Scattering of Light*, translated from Russian by R. T. Beyer (Plenum, New York, 1968).
³R. S. Finn and J. F. Ward, *Phys. Rev. Lett.* **26**, 285 (1971); *J. Chem. Phys.* **60**, 454 (1974).
⁴J. F. Ward and I. J. Bigio, *Phys. Rev. A* **11**, 60 (1975); C. K. Miller and J. F. Ward (unpublished).
⁵J. F. Ward and G. H. C. New, *Phys. Rev.* **185**, 57 (1969).
⁶A. D. Buckingham and B. J. Orr, *Trans. Faraday Soc.* **65**, 673 (1969).
⁷J. M. Brown, A. D. Buckingham, and D. A. Ramsey, *Can. J. Phys.* **49**, 914 (1971).
⁸S. E. Harris and D. M. Bloom, *Appl. Phys. Lett.* **24**,

- 229 (1974).
⁹E. A. Stappaerts, S. E. Harris, and J. F. Young, *Appl. Phys. Lett.* **29**, 669 (1976).
¹⁰K. S. Krishnan, J. S. Ostrem, and E. A. Stappaerts, *Opt. Eng.* **17**, 108 (1978).
¹¹H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.* **43**, S34 (1965).
¹²P. W. Langhoff, J. D. Lyons, and R. P. Hurst, *Phys. Rev.* **148**, 18 (1966); E. Leuliette-Devin and R. Locqueneux, *Chem. Phys. Lett.* **19**, 497 (1973); R. E. Sitter and R. P. Hurst, *Phys. Rev. A* **5**, 5 (1972).
¹³J. M. O'Hare and R. P. Hurst, *J. Chem. Phys.* **46**, 2356 (1967); A. D. McLean and M. Yoshimine, *ibid.* **45**, 3467 (1966); **46**, 3682 (1967); S. P. Liebmann and J. W. Moskowitz, *ibid.* **54**, 3622 (1971).

- ¹⁴G. P. Arrighini, M. Maestro, and R. Moccia, Symp. Faraday Soc. 2, 48 (1968).
- ¹⁵P. Lazzeretti and R. Zanasi, Chem. Phys. Lett. 39, 323 (1976).
- ¹⁶P. A. Christiansen and E. A. McCullough, Chem. Phys. Lett. 63, 570 (1979).
- ¹⁷P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).
- ¹⁸H. J. Werner and W. Meyer, Mol. Phys. 31, 855 (1976).
- ¹⁹P. A. Christiansen and E. A. McCullough, Chem. Phys. Lett. 51, 468 (1977).
- ²⁰A. J. Sadej, Chem. Phys. Lett. 47, 50 (1977).
- ²¹R. J. Bartlett, J. C. Bellum, and E. J. Brandas, Int. J. Quantum Chem. 7S, 449 (1973).
- ²²J. E. Gready, G. B. Bacsikay, and N. S. Hush, Chem. Phys. 23, 9 (1977); 22, 141 (1977).
- ²³K. A. Brueckner, Phys. Rev. 97, 1353; 100, 36 (1955); J. Goldstone, Proc. R. Soc. A 239, 267 (1957).
- ²⁴H. P. Kelly, Adv. Chem. Phys. 14, 129 (1969); Phys. Rev. 131, 684 (1963); 136, 896 (1964).
- ²⁵R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. 14, 561 (1978).
- ²⁶R. J. Bartlett and I. Shavitt, Chem. Phys. Lett. 50, 190 (1977); 57, 157 (1978).
- ²⁷R. J. Bartlett and D. M. Silver, Int. J. Quantum Chem. Symp. 9, 183 (1975); Phys. Rev. A 10, 1927 (1974).
- ²⁸J. Cizek, J. Chem. Phys. 45, 4256 (1966); Adv. Chem. Phys. 14, 35 (1969).
- ²⁹J. Paldus, J. Cizek, and I. Shavitt, Phys. Rev. A 5, 50 (1972).
- ³⁰L. T. Redmon, G. D. Purvis, and R. J. Bartlett, J. Chem. Phys. 69, 5386 (1978).
- ³¹C. Möller and H. S. Plesset, Phys. Rev. 46, 618 (1934).
- ³²J. Goodisman and W. Klemperer, J. Chem. Phys. 38, 721 (1963).
- ³³S. Fraga and G. Malli, *Many-Electron Systems: Properties and Interactions* (Saunders, Philadelphia, 1968).
- ³⁴T. C. Caves and M. Karplus, J. Chem. Phys. 50, 3649 (1969).
- ³⁵H. Peng, Proc. R. Soc. A 178, 499 (1941); A. Dalgarno, Adv. Phys. 11, 291 (1962); S. Kaneko, J. Phys. Soc. Jpn. 14, 1600 (1959); L. C. Allen, Phys. Rev. 118, 167 (1960); R. M. Stevens and W. N. Lipscomb, J. Chem. Phys. 40, 2238 (1964); 41, 184 (1964).
- ³⁶R. J. Bartlett and H. Weinstein, Chem. Phys. Lett. 30, 441 (1975); T. S. Nee, R. G. Parr, and R. J. Bartlett, J. Chem. Phys. 64, 2216 (1976).
- ³⁷L. Adamowicz and A. J. Sadej, Chem. Phys. Lett. 53, 377 (1978).
- ³⁸D. J. Thouless, *Quantum Mechanics of Many Body Systems* (Academic, New York, 1961).
- ³⁹M. J. Jamison, Int. J. Quantum Chem. Symp. 4, 103 (1971).
- ⁴⁰G. D. Purvis and R. J. Bartlett, J. Chem. Phys. 68, 2114 (1978).
- ⁴¹T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).
- ⁴²S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).
- ⁴³T. H. Dunning, J. Chem. Phys. 55, 3958 (1971).
- ⁴⁴The UMBPT program which does MBPT and coupled cluster calculations is authored by R. J. Bartlett and G. D. Purvis. The SCF calculations and integral transformations are accomplished by the program GRNFNC, authored by G. D. Purvis. The molecular integral program used is MOLECULE, authored by Jan Almlöf.
- ⁴⁵R. J. Bartlett and G. D. Purvis, *Physica Scripta*, to be published.

APPENDIX B

MOLECULAR HYPERPOLARIZABILITIES

II. A CORRELATED STUDY OF H₂O*

George D. Purvis III

and

Rodney J. Bartlett

(Submitted for publication, Phys. Rev. A)

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

*This research was sponsored by the U.S. Office of Scientific Research under Contract No. F49620-78-C-0046. The United States Government is authorized to reproduce and distribute reprints for government purposes notwithstanding any copyright notation hereon.

ABSTRACT

Correlated calculations using many-body perturbation theory and good basis sets for the dipole moment, polarizability, and hyperpolarizabilities of H₂O are reported. The finite field, coupled Hartree-Fock theory is used as a zeroth-order approximation, with electron correlation included via the linked-diagram theorem. Single-, double-, and quadruple-excitations contribution are included. It is found that correlation changes $|\beta(\omega=0)|$ by about 50 percent compared to the CHF result. Even larger changes are found among the components of γ . The dependence of the β hyperpolarizability on geometric displacements is investigated, finding that β can be highly sensitive to slight changes in bond lengths.

I. INTRODUCTION

In previous work,⁽¹⁾ hereafter called I, a correlated study of the HF molecule employing many-body perturbation theory (MBPT) of the dipole moment, μ , and the polarizability and hyperpolarizability tensors α , β , and γ was reported. The objective of that study was to investigate the dependence of hyperpolarizabilities on normal basis sets of contracted gaussian type (CGTO) and to assess the effect of correlation on the predictions of these quantities. Basis sets were chosen by using the criteria that good agreement should be achieved between the predictions of the finite basis sets and numerical Hartree-Fock calculations of the z-components of the higher polarizabilities.^(1,2) Although other components are not sampled, this procedure hopefully provides some reason to believe that the basis sets used would at least be adequate to provide a reasonable estimate of the correlation effects in hyperpolarizabilities. In I, correlation was found to change μ_z , $\bar{\alpha}$, $\beta = (\beta_{zzz} + \beta_{yyz} + \beta_{xxz})$, and γ_{zzzz} , by 6.5%, 14%, 28% and 39% respectively, which suggests that non-correlated predictions of hyperpolarizabilities are unlikely to provide reliable agreement with experiment.

In the case of HF, no experimental values are available, hence it is of interest to apply the techniques developed in I to make predictions of the hyperpolarizabilities of H₂O. Experimental values obtained by dc -induced second harmonic generation experiments⁽³⁾ are available for H₂O⁽⁴⁾ yet previous⁽⁵⁻⁷⁾ non-correlated theoretical calculations have not been able to provide reasonable agreement.

In this paper we report a series of computations in different basis sets for the H₂O molecule ranging in size from 50 to 75 GCTO's. In addition, we study the dependence of hyperpolarizabilities on vibrational stretching and

bending motions, and find a surprising degree of dependence of β on the symmetric stretching mode of H_2O .

II. SYNOPSIS OF THEORETICAL CALCULATIONS

The notation and details of the theory are reported in I. Briefly, we consider the energy in the presence of an electric field \underline{E} ,

$$\begin{aligned} W(\underline{E}) = W(0) - \mu_i E_i - (2!)^{-1} \alpha_{ij} E_i E_j - (3!)^{-1} \beta_{ijk} E_i E_j E_k \\ - (4!)^{-1} \gamma_{ijkl} E_i E_j E_k E_l \dots \end{aligned}$$

where summation over repeated indices is assumed. The induced dipole moment is obtained as the derivative, $-(\frac{\partial W}{\partial E_i})$.

In this work finite field techniques are used, where $W(\underline{E})$ is computed at a series of field strengths from which the various components in the expansion in Eqn. (1) can be obtained. The finite field strengths are chosen symmetrically (e.g. ± 0.01) which enables one to eliminate the next higher term in the series, and thereby the principal contaminating effect, by taking odd and even combinations of the finite-field energies.(1)

The energies are obtained from the linked-diagrams theorem of MBPT(8-10) to be

$$W(\underline{E}) = W_{CHF}(\underline{E}) + \sum_{K=1}^{\infty} \langle \phi_0(\underline{E}) | V(\underline{E}) [(W_0(\underline{E}) - F(\underline{E}))^{-1} V(\underline{E})]^K | \phi_0(\underline{E}) \rangle_L \quad (2)$$

$F(\underline{E})$, the Fock hamiltonian plus the one-electron perturbation due to the electric field, serves as the unperturbed problem, while $V(\underline{E})$ is the correlation perturbation. $V(\underline{E})$ is also field dependent due to its including the effective SCF potential. $W_0(\underline{E})$ is the sum of the field dependent orbital energies associated with the one-electron SCF hamiltonians that compose $F(\underline{E})$. $\phi_0(\underline{E})$ is the finite-field SCF solution. The unperturbed result in this scheme is

the coupled Hartree-Fock (CHF) solution. Notice, in a double perturbation approach relative to the field-free SCF solution, the CHF result corresponds to the sum of an infinite series of MBPT diagrams⁽¹¹⁾. Hence, the present approach deals with "dressed" diagrams relative to the double perturbation approach. In this work, all possible diagrams that arise through fourth-order that involves single, double, or quadruple (i.e. fourfold) excitations are included in the calculation of $W(E)$, while those fourth-order diagrams that have threefold excitations are neglected. This model is referred to as SDQ-MBPT(4).^(1,10,12)

III. RESULTS AND DISCUSSION

A. Previous Results

The electric susceptibility $\chi_{11}^{(2)}$ for H_2O has been determined from dc-induced second-harmonic generation experiments by Ward and Miller to be -94 ± 4 esu/molecule.⁽⁴⁾ This value is frequency dependent, but it is expected that this result should be within about 10 percent of the static value. Hence, $\chi_{11}^{(2)} \approx 10/3 \beta(\omega=0) = 10/3(\beta_{zzz} + \beta_{xxz} + \beta_{yyz})$. The minus sign signifies that β is opposite in direction to the permanent dipole moment of H_2O , assumed to be in the direction $O^-H_2^+$.

Several previous calculations of β at the uncoupled Hartree-Fock (UCHF) and coupled Hartree-Fock (CHF) level have been reported.⁽⁵⁻⁷⁾ Liebman and Moskovitz obtain +90.6 in a UCHF calculation for $\chi_{11}^{(2)}(\omega=0)$ ⁽⁵⁾, where the sign seems to be in error.⁽⁴⁾ Arrighini, et. al.⁽⁶⁾ report CHF values of -51.6 and -48.0 in (2s1p|1s) and (5s3p1d|2s1p) Slater (STO) basis sets, respectively. In the larger STO basis, the hydrogen components perpendicular to the plane are omitted. It is a common result that $|\beta|$ is smaller when a better basis set is used, although the reduction in $|\beta|$ is usually more dramatic^(1,7) than is this example.

Lazzaretti and Zanasi report CHF calculations of β for H_2O for three contracted gaussian orbital (CGTO) basis sets,⁽⁷⁾ ranging from minimum (2s1p|1s), to double zeta (4s 2p|2s), to a polarized double zeta (4s12p1d|2s1p) basis set. The values for $\chi_{11}^{(2)}(\omega=0)$ are respectively, -52.5, -79.2, and -21.9. Again the general trend that a better basis reduces CHF values of $|\beta|$ is evident, emphasizing the accidental agreement between experiment and the double-zeta basis. Unfortunately, the very accurate, large basis results of Werner and Meyer⁽¹³⁾

for the dipole moment and polarizability are not extended to predictions of hyperpolarizabilities, since these authors correctly question whether even basis sets much larger than those used in the previous studies can be expected to have any validity for properties as sensitive as hyperpolarizabilities.⁽¹³⁾

In I we showed that correlation and basis sets can have a very large effect on ab initio predictions of hyperpolarizabilities, so it is of interest to use the same techniques to attempt to make some assessment of the capability of theory to accurately predict hyperpolarizabilities. The present study will focus on three elements: correlation, basis sets, and the dependence of β on changes in molecular geometry.

B. Basis Sets

In this work, four different basis sets are considered, all larger than those previously used in studies of H₂O hyperpolarizabilities. The prescription used is essentially that of Christiansen and McCullough.⁽²⁾ The first three basis sets, A, B, and C are built from Dunning's 5s3p contraction⁽¹⁴⁾ of Huzinaga's primitive 9s5p basis set for the oxygen atom,⁽¹⁵⁾ and Dunning's 3s contraction for hydrogen. These functions are augmented by a 3d gaussian polarization function on oxygen (all six components) (exponent - 1.211) and a p gaussian polarization function (exponent - 0.761) on hydrogen. This (5s3p¹d|3s1p) basis is considered to be generally adequate to describe the basic molecular charge density, but insufficient for predictions of polarizabilities. To assist in describing such additional properties, the basis is augmented by adding an extra set of s, p, and d functions to oxygen with the

exponents chosen to have the same ratio as the last two functions of each type, generally a factor of about 0.3 times the previous exponent. Similarly, hydrogen is augmented by an s and a p function whose exponents are chosen in the same manner. This results in basis A, a $(6s4p2d|4s2p)$ basis of 50 CGTO. It is expected that this basis should be generally reliable for polarizabilities, but not hyperpolarizabilities where at least another shell of functions with increasingly diffuse exponents is recommended. By proceeding in this manner, an additional set of s,p, and d functions are added to oxygen, and an additional s and p function to hydrogen. This constitutes basis B, a $(7s5p3d|5s3p)$ basis of 68 CGTO. To add additional diffuseness to the charge cloud, a third basis, basis C, includes an additional s (exponent 0.0079) and p function (exponent 0.0057) located at the center-of-mass of the molecule. This $(7s5p3d|5s3p;1s1p)$ basis requires 72 CGTO.

The construction of the basis sets A, B, and C emphasizes the long-range, tail region of the molecule where more and more diffuse functions are employed to try to describe this part of the charge density. In I we found that by comparison with numerical Hartree-Fock calculations of the on-axis components of the polarizability and hyperpolarizabilities, it is also important to have a basis that is capable of describing the small differences in the charge density in regions moderately near the nuclei. Since our basis in I is successful in obtaining quite good agreement with the numerical Hartree-Fock results, we also have used this procedure to construct a fourth-basis set, D, that we hope will retain some of the apparent reliability of the previous work.

This basis starts with Dunning's $(4s3p|2s)$ contraction, then uses a d-polarization function defined as a two gaussian fit⁽¹⁴⁾ to a Slater exponent of

3.0175. The smaller exponent is then multiplied by 0.4 to generate a new d-orbital exponent. Two successive sets of d-functions are obtained by a repetition of this scheme. Similarly, a fourth p-function (exponent 0.2137) is added to oxygen, and two more p-functions with exponents chosen to be 0.4 times and then $(0.4)^2$ times this value. Also, two s-functions are added by taking 0.4 and $(0.4)^2$ times the smallest s-exponent (i.e., 0.2846). Two additional s-functions are added to hydrogen (exponents 0.1776 and 0.04932) and a 2p polarization function two gaussian fit⁽¹⁴⁾ to an STO exponent of 2.047, and an additional p-function with exponent (0.2174). The resulting basis of 65 CGTO is of the form $(6s5p4d|4s2p)$. The differences in the construction of this basis compared to A, B, and C should not be major, but are of interest in assessing the sensitivity of the predictions to modest changes in basis set, and for comparisons with the previous results for HF.⁽¹⁾

C. Results

In Table I are listed CHF results for μ , α , β , and γ for the basis sets A-D. Since bases B and C are constructed from basis A by simply adding additional diffuse functions without any other change, it is possible to form some assessment of the effect this augmentation has on the predicted results.

The largest change is found in the components of $|\beta|$, reducing their size as has been observed to usually be the case when a better basis set is employed. Also, since the second-harmonic generation experiment gives a $|\beta|$ larger than the theoretical predictions, improving the basis set further destroys any fortuitous agreement between the CHF results and experiment. The highly diffuse functions included in basis C, but not B, are observed to have only a small effect on β .

A significant, but smaller change occurs in the values of α between basis A and B, although the dipole moment is little modified. Again, the extra diffuse functions in C have little effect on α and none on μ . The change in α between A and B is consistent with the observation of Werner and Meyer⁽¹³⁾ (WM) that at least a 3d basis set is necessary to simultaneously describe the energy, dipole moment, and polarizability. In fact, for H₂O WM recommend the d-orbital exponents 0.10, 0.30, and 1.20, while our basis B uses the quite similar though independently arrived at values of 0.11, 0.37, and 1.211.

The main problem in basis sets A, B, and C is found in the dipole moment. Although there is little change when more diffuse functions are added, its value is still rather far from the WM CHF result of $\mu_z = 0.782$.

Consequently, the failure of bases A-C to account for this result, appears to lie among the interior basis functions rather than the more diffuse functions. Since β tends to be sensitive to both interior and tail regions of the charge density, in hopes of obtaining more reliable results for β , we focus on a slightly modified approach to generating a basis set for hyperpolarizabilities that we found to be successful for HF,⁽¹⁾ which gives basis set D. This basis uses a two gaussian fit for the tight d-function, and an additional diffuse d-orbital, as well as some other, presumably less significant changes. In Table I it may be seen that for basis D, μ , and α are in excellent agreement with the WM results of $\mu = 0.782$, and $\alpha_{zz} = 8.47$, $\alpha_{yy} = 9.04$, and $\alpha_{xx} = 7.99$. As observed by WM the polarizability is less sensitive to such a change than is the dipole moment.

Again, as in the transition from A to B and C, basis D further reduces the components of β . It is not appropriate to claim any basis set convergence from these four sets of CHF calculations, but experience strongly indicates that some basis set limit convergence would tend to predict even smaller $|\beta|$ at the CHF level, further destroying any agreement between the CHF predictions and experiment. To rectify this dilemma, three features can be addressed that can increase $|\beta|$. These are correlation, geometric displacement as might become important in higher temperature experiments, and the frequency dependence. In this paper we will consider the first two possibilities with frequency dependence to be studied in future work.

Considering the second possibility, first, Figures 1 and 2 illustrate the dependence of two components of β on the symmetric stretch and bending mode in H₂O. These CHF calculations use basis C. The values $\langle \Delta R_1^2 \rangle^{1/2} = 0.128b$

$\langle \Delta O^2 \rangle^{1/2}$ = 8.72 are the experimental root-mean-square amplitudes for H₂O displacement coordinates, at 0K. (16,17) The values of $\langle \Delta R_1 \rangle$ = 0.0266 and $\langle \Delta O \rangle$ = 0.183 degrees. It is apparent that there is a very steep dependence of β_{yyz} and β_{zzz} on the stretch, although not the bending mode. In the case of β_{xxz} , its value is comparatively unaffected, changing from +0.26 at $r_e +0.128$ a.u. to -0.68 at r_e and +1.15 at $r_e -0.128$ a.u.

Judging from Figures 1 and 2, the zero-point correction of $\beta = (\beta_{zzz} + \beta_{xxx} + \beta_{yyz})$ amounts to about 1.7 units. The sensitivity of β_{zzz} and β_{yyz} to displacements, however, suggests that experiments conducted at elevated temperatures involving higher rotational states, should be correlated for excited state populations and centrifugal distortion of bond lengths.

The change in β with displacement is more extreme than is the change in α . The mean polarizability assumes the values 8.54 at r_e , and 7.76 at $R_e - \delta R$, and 9.47 at $R_e + \delta R$. In the case of the bending mode, $\bar{\alpha} = 8.52$ at $\theta_e - \delta \theta$ and 8.60 at $\theta_e + \delta \theta$.

The other element that is important in making accurate predictions of static hyperpolarizabilities is electron correlation. In Table II are listed the CHF and correlated SDQ-MBPT(4) results for basis sets A and D, with experimental values where available.

The effect of correlation changes the CHF dipole moment in basis D by ~6 percent, $\bar{\alpha}$ by ~9 percent and β by ~50 percent. Similarly large changes in the various components of χ of ~36 to 85 percent are observed. In the case of HF, similar values of ~6 percent, ~14 percent, 28 percent, and 39-to-75 percent are found.⁽¹⁾ In μ , α , β , and χ the effect of correlation is

approximately the same as the basis set effect between bases A and D. In the case of $\underline{\mu}$, $\underline{\alpha}$, and $\underline{\gamma}$ the basis set effect and the effect of correlation are additive, but for $\underline{\beta}$ this is not at all the case.

The delicate balance between basis set and correlation needed to describe β accurately, has mixed effects. Since a larger correlation correction will typically be obtained in a better basis set, as the basis is improved, the observed reduction in the CHF $|\beta|$ will probably be largely offset by the greater correlation contribution. This has the implication that some hope exists for obtaining a reasonable level of convergence with basis sets for predictions of $|\beta|$. However, at the CHF level, no such possibility persists. On the other hand, the sensitivity of β to both basis sets and correlation emphasizes the importance of treating both aspects of the problem in a balance fashion, and at a higher level of sophistication.

The results of basis D in Table II correspond to an electric susceptibility $\chi_{11}^{(2)}(\omega=0)$ of -66 at r_e and -74 at r_0 , still about 21 percent different than the frequency dependent SHG results of $-94+4$. It is clear, however, that what agreement there is between experiment and prior CHF calculations⁽⁵⁻⁷⁾ has to be essentially accidental.

In Table III are reported the individual correlation corrections to $\underline{\mu}$, $\underline{\beta}$, and $\underline{\gamma}$. As in the prior study of HF, second-order perturbation theory provides most of the correlation contribution. Since in the finite-field approach used in this work, most of the single excitations effects that are quite important for one-electron operators are incorporated into the CHF (unperturbed) results, most important correlation effects are due to

double-excitation relative to field-dependent orbitals, which are exclusively responsible for second- and third-order perturbation theory. In fourth-order, the residual effects of single excitations first appear, and their value is slightly larger than the fourth-order double excitation contribution. As in I, the quadruple excitation fourth-order diagrams contribute very little to the correlated result.

In summary, the importance of electron correlation to predictions of hyperpolarizabilities has been emphasized. Correlation effects make a contribution that significantly increases $|\beta|$ and the components of γ . Since the experimental values for $|\beta|$ are normally larger than the theoretical predictions, correlation can make an important contribution toward resolving this discrepancy. It is fairly clear, that CHF results can at best offer fortuitous agreement with experiment when inferior basis sets are used. We have also shown that the β_{γ} hyperpolarizability can be very sensitive to small displacements of the nuclei in a molecule. This sensitivity should be considered in future theoretical calculations and can be a source of error in comparing with the experimental results. The remaining major question to resolve, is the change in β with frequency. That feature, too, should increase the $|\beta|$ obtained in theoretical calculations. When this element is included, perhaps reasonable agreement between ab initio calculations and experiment will finally become possible.

REFERENCES

1. R. J. Bartlett and G. D. Purvis, Phys. Rev. A20, 1313 (1979).
2. P. A. Christiansen and E. A. McCullough, Chem. Phys. Letters, 63, 570 (1979); 51, 468 (1977).
3. J. F. Ward and G. H. C. New, Phys. Rev. 185, 57 (1969).
4. J. F. Ward and C. K. Miller, Phys. Rev. 19, 826 (1979)
5. S. P. Liebmann and J. W. Moskowitz, J. Chem. Phys. 54, 3622 (1971).
6. G. P. Arrighini, M. Maestro, and R. Moccia, Symp. Faraday Soc. 2, 48 (1968).
7. P. Lazzaretti and R. Zanasi, Chem. phys. Letters 39, 323 (1976).
8. K. A. Brueckner, Phys. Rev. 97, 1353; 100, 36 (1955); J. Goldstone, Proc. R. Soc. A239, 267 (1957).
9. H. P. Kelly, Adv. Chem. Phys. 14, 129 (1969).
10. R. J. Bartlett and G. D. Purvis, Intern. J. Quantum Chem. 14, 561 (1978).
11. T. C. Caves and M. Karplus, J. Chem. Phys. 50, 3649 (1969).
12. R. J. Bartlett and G. D. Purvis, Physica Scripta 21, 255 (1980).
13. H. J. Werner and W. Meyer, Mol. Phys. 31, 855 (1976).
14. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970); 55, 3958 (1971).
15. S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).
16. K. Kuchitsu and L. S. Bartell, J. Chem. Phys. 36, 2460 (1962).
17. W. C. Ermler and C. W. Kern, J. Chem. Phys. 55 4851 (1971); S. J. Cy in, Molecular Vibration and Mean Square Amplitudes, Elsevier, Amsterdam, 1968, p. 205.

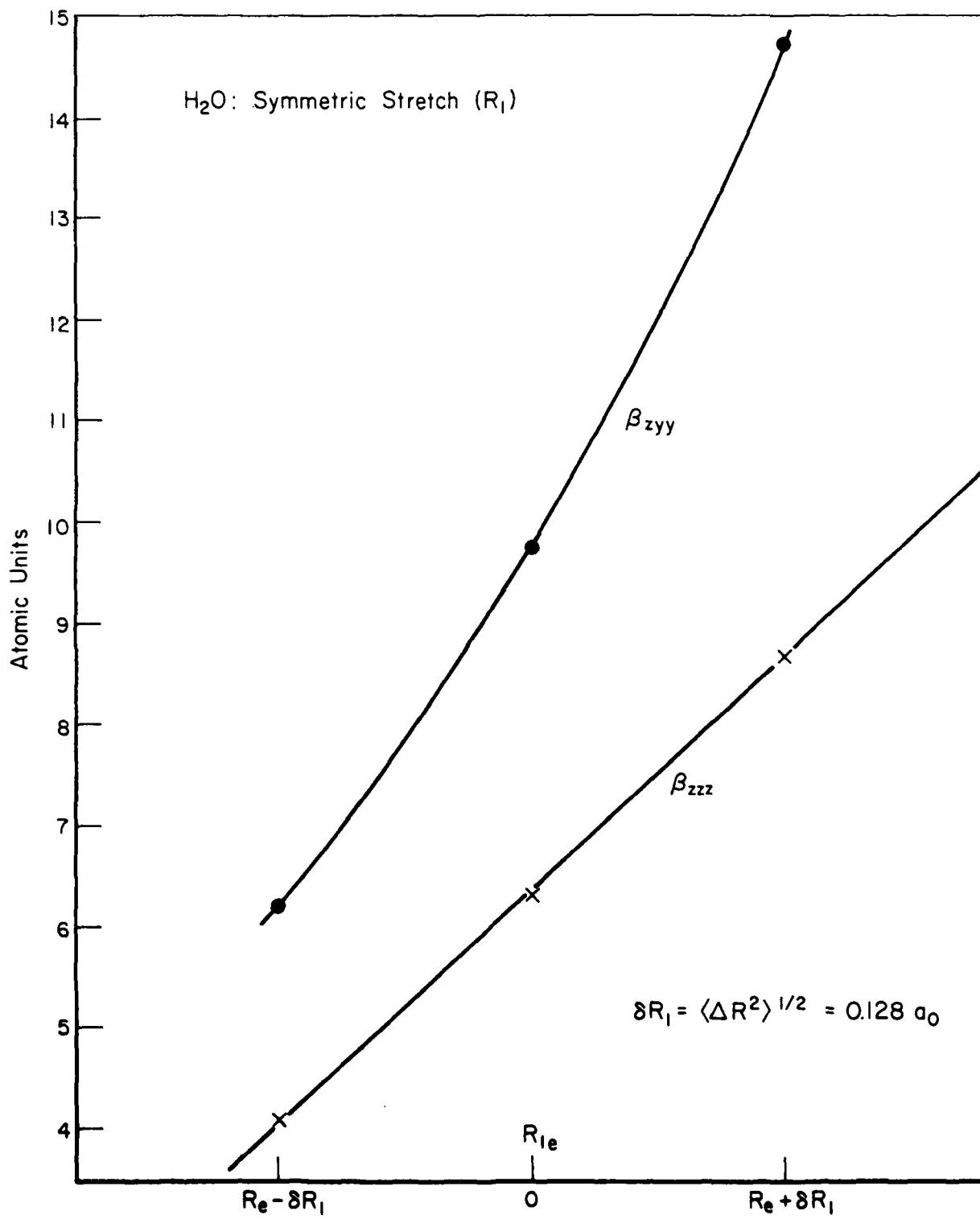


FIGURE 1. DEPENDENCE OF THE β_{zzz} AND β_{zyy} COMPONENTS OF THE HYPERPOLARIZABILITY ON THE SYMMETRIC STRETCH OF H₂O. CHF CALCULATIONS, BASIS C. .

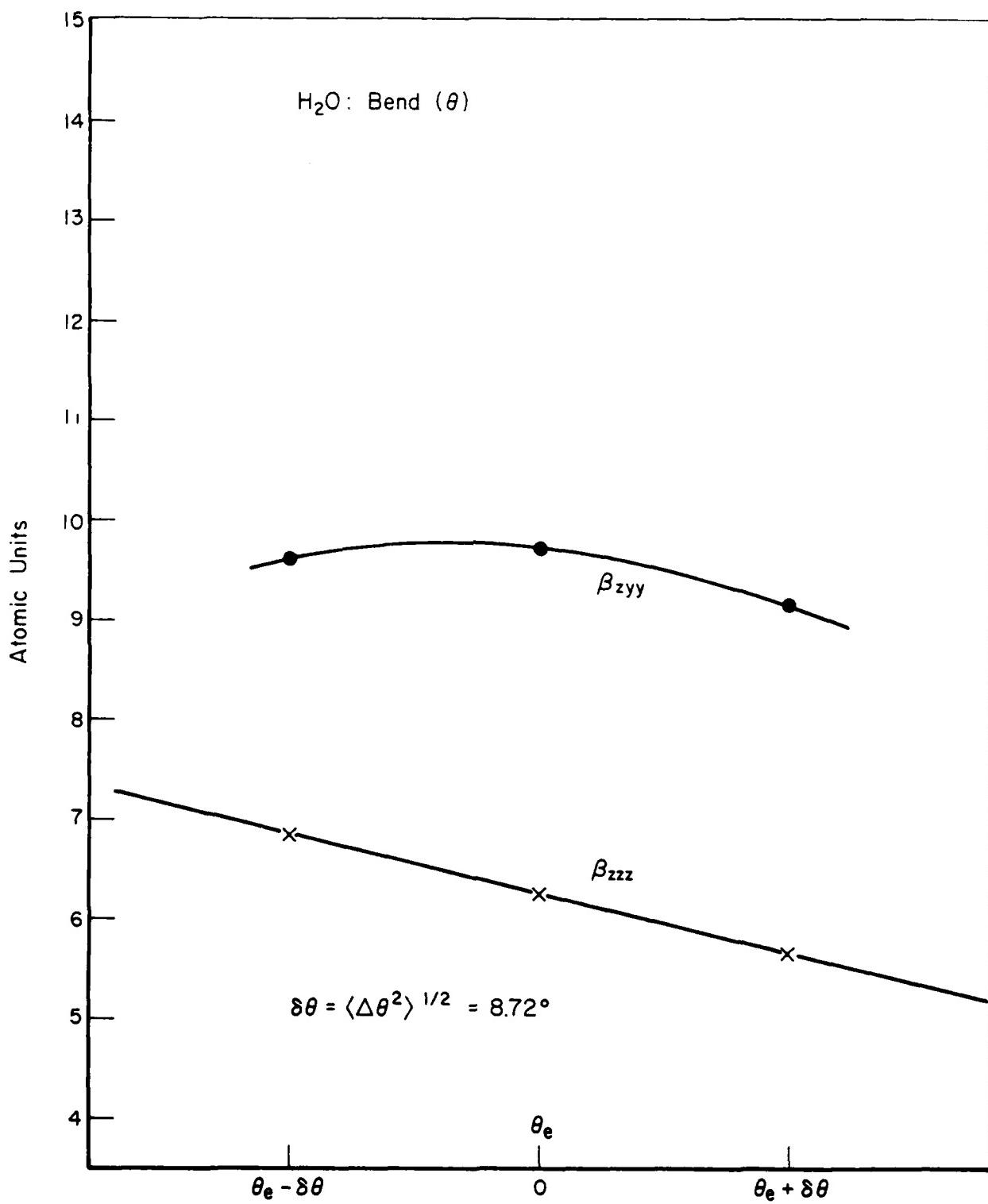


FIGURE 2. DEPENDENCE OF THE β_{zzz} AND β_{zyy} COMPONENTS OF THE HYPERPOLARIZABILITIES ON THE BENDING MODE OF H_2O . CHF CALCULATIONS, BASIS C.

TABLE I. DIPOLE MOMENT AND FIRST, SECOND, AND THIRD ORDER POLARIZABILITIES FOR H₂O DETERMINED BY COUPLED-HARTREE-FOCK THEORY (Molecule is in zy-plane, with z the molecular axis. Orientation is O-H₂ defined as a positive dipole moment; r_{OH} = 1.811b, θ = 104.5°)

Basis Set	A ^a	B ^b	C ^c	D ^d
μ_z	0.807	0.796	0.796	0.784
α_{zz}	8.01	8.50	8.55	8.47
α_{yy}	8.78	9.11	9.12	9.18
α_{xx}	7.21	7.96	7.95	7.95
β_{zzz}	-8.08	-6.65	-6.31	-5.22
β_{yyz}	-12.86	-10.03	-9.75	-9.63
β_{xxz}	0.	0.85	-0.68	-0.48
γ_{zzzz}	490	-	-	770
γ_{yyzz}	-	-	-	270
γ_{xxzz}	-	-	-	350
γ_{xxxx}	-	-	-	1400
γ_{yyyy}	-	-	-	460
γ_{xxyy}	-	-	-	-

^a Basis A is (6s4p2d|4s2p), $W_{SCF}^{(o)} = -76.05391$.

^b Basis B is (7s5p3d|5s3p), $W_{SCF}^{(o)} = 076.05412$.

^c Basis C is (7s5p3d|5s3p;1s1p); $W_{SCF}^{(o)} = -76.05420$.

^d Basis D is (6s5p4d|4s2p); $W_{SCF}^{(o)} = -76.05443$.

TABLE II: EFFECT OF CORRELATION ON PREDICTED DIPOLE MOMENT, POLARIZABILITY AND HYPERPOLARIZABILITIES OF H₂O (values in atomic units)

	CHF		SDQ-MBPT(4)			
	A ^a (r _e)	D ^a (r _e)	A ^a (r _e)	D ^a (r _e)	D ^b (r ₀)	Experiment
w(0)	-76.05391	-76.05443	-76.29481	-76.29898	...	-76.374 ^c
w _{corr}	---	---	-0.2409	-0.2446c	...	0.306 ^c
μ	0.807	0.784	0.758	0.735	0.737	0.724 ^d
α_{zz}	8.01	8.47	8.77	9.46	9.64	-
α_{yy}	8.78	9.18	9.49	9.87	10.07	-
α_{xx}	7.21	7.95	7.73	9.30	9.38	-
$\gamma = 1/3(\alpha_{zz} + \alpha_{yy} + \alpha_{xx})$	8.0	8.7	8.7	9.5	9.7	9.82 ^e
β_{zzz}	-8.1	-5.2	-11.5	-9.2	-9.8	-
β_{zyy}	-12.9	-9.6	-14.3	-10.0	-12.3	-
β_{zxx}	0	-0.5	-1.9	-3.7	-3.5	-
$\beta = (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})$	-21.0	-15.3	-27.7	-22.9	-25.6	-32.7 ^f
γ_{zzzz}	490.	700	700	1230	1300	-
γ_{yyyy}	-	460	-	630	...	-
γ_{xxxx}	-	1400	-	2580	...	-
γ_{zzyy}	-	270	-	400	...	-
γ_{zxxx}	-	360	-	630	...	-

Footnotes (Table II.)

a Calculations in basis sets A and D are at $r_e = 1.811$ a.u. and $\theta = 104.5^\circ$.

b ($r_0 = 1.8376$, $\theta_0 = 104.63$); these values are estimated from linear extrapolation of calculations at a symmetric stretch of $r_e + 0.079$ a.u.

c The experimental value is the estimated RHF limit of J. A. Pople and J. J. Binkley Molec. Phys. 29, 599 (1975), plus the estimated valence correlation energy. All correlation contributions are obtained by freezing the $1s^2$ oxygen core electrons at the SCF level.

d A. L. McClellan, Tables of Experimental Dipole Moments, 1963, Freeman and Co.

e Reference 13.

f Reference 4. This is a frequency dependent result.

TABLE III. INDIVIDUAL CORRELATION CORRECTIONS FOR THE DIPOLE MOMENT AND HYPERPOLARIZABILITIES (atomic units)

